AIR QUALITY STUDY IN THE LOWER TAMAR VALLEY, TASMANIA

by

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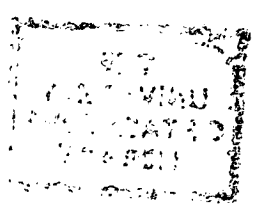

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CHAPTER 5 AMBIENT AIR MONITORING IN THE LOWER TAMAR VALLEY

5.1 Introduction

An air quality study for an industrial area requires not only a good understanding of the meteorological processes which greatly affect the dispersion of air pollutants from various sources, but also a good knowledge of the existing quality of ambient air so that the impact of air pollution, if any, on the physical and human environment can be assessed.

The knowledge of the quality of the ambient air can be acquired through 'monitoring', which is defined by Bryan (1976) as "any systematic, planned means of determining the quality of air using whatever methods are consistent with the obtaining of data over a reporting interval and at a frequency of collection required by the monitoring objectives involved". Monitoring is an integral part of air quality management, and, as discussed by Bryan (1976), it serves the following objectives:

(1) Obtaining background data - Background data in an area may be required to determine the existing level of air pollution.

(2) Trend evaluation - To provide long term information so that the trend of air pollution in an area can be evaluated.

(3) Acute incident warning - To provide a warning about a possible effect of an air pollutant or pollutants in any acute incident.

(4) Standard or criteria evaluation - To provide a guide for defining acceptable air quality so that legal standards and criteria can be designed.

(5) Source detection - To determine the quantitative effects on an area immediately surrounding a known source of pollution.

(6) Effects surveillance - To determine the effects of air pollution in terms of number and distribution of receptors, suspected nature and severity of effect, time-dosage aspects of expected effect, and presence of confounding factors.

(7) Evaluation of atmospheric process - As many air pollutants

undergo physical and chemical changes during their residence time in the atmosphere, monitoring is required to evaluate the dynamics of the processes so that they can be better understood.

Apart from these, air monitoring has now become an essential tool in the investigation of long range transport, and network measurements are made in many countries, especially in North America and Europe (Whelpdale and Barrie, 1981). The actual concentrations of air pollutants in the long range transport are generally small and nearly always below air quality levels; thus it is the long-term accumulation by deposition that is important (Pankrath, 1982).

However, ambient air monitoring can be a very expensive exercise, and it can cost millions of dollars particularly if a proper network which gives continuous measurements is to be set up, such as those in the Latrobe Valley in Victoria and the Hunter Valley in New South Wales. With the constraints of the financial and human resources, the ambient air monitoring programme in this study was very modest indeed by the standards of others on the mainland. It was decided to adopt the most conventional, simple, and economical methods which could achieve reasonably reliable results given that the measurements are conducted properly.

As outlined in Chapter 3, the ambient air monitoring programme in this study is divided into three categories:

(1) atmospheric deposition (or dust fallout);

(2) wet-only precipitation; and

(3) suspended particulates.

Through the collection and chemical analyses of all these samples (the techniques are described in Sections 3.5 to 3.9 of Chapter 3), it was intended to give a preliminary assessment of the ambient air quality in the lower Tamar Valley, particularly the Bell Bay industrial area, during the study period. Thus, while some of the objectives as outlined by Bryan (1976) can only be touched upon, some cannot be achieved because of the time constraint of this study.

This chapter presents and discusses all the ambient air data collected during the study period. The data will be compared with those available in literature wherever possible. The spatial and temporal variations of the deposition rates of insoluble dust, major trace

elements and acidic species, as well as the concentrations of the suspended particulates in the lower Tamar Valley are investigated, and statistically correlated. Attempts are also made to correlate the distribution of the chemical compositions of the various collected samples with the operations of the various industrial sources, as well as the prevailing meteorological parameters such as wind vectors, atmospheric stability, and temperature inversions in the area. A combination of chemical analytical techniques was used. AAS was used to analyse and characterise the various trace metals in all samples, supplemented by SEM/EDAX for the suspended particulates samples, and FT-IR for the precipitation samples.

The ambient air quality of an industrial area varies from time to time, as it is a function of many variables such as meteorological conditions, production activities of the industries, application of any air pollution control, etc.

5.2 Dust Fallout and Its Yardstick

The atmospheric deposition monitoring programme was the first to be carried out because it requires only simple equipment. The total insoluble dust obtained from the deposition samples, expressed in mg m^{-2} day^{-1}, could be used to indicate the degree of dustiness at a location (Ayling and Bloom, 1976; Low, 1980). Currently there are no legal limits or guidelines for 'acceptable' dustfall rates in rural, residential, light or heavy industrial areas in Tasmania, hence it is difficult to assess the adverse effects of dust pollution in the study area. However, some guidelines have been provided both overseas and in other states of Australia. For example, Williams and Edmisten (1965), after studying the air quality in metropolitan Nashville, USA, recommended a maximum permissible dustfall level of 130 mg m^{-2} day^{-1} (averaged over a year), based on the figure for the water-insoluble components. Dr. S.R. Craxford of the British Warren Spring Laboratory believes that the average urban grit and dustfall of 113 mg m^{-2} day^{-1} is a minor drawback of town life; a figure exceeding 200 mg m^{-2} day^{-1} makes a locality "unpleasantly dusty"; and a figure about 300 mg m^{-2} day^{-1} indicates "gross pollution" (Gilpin, 1978). Cantrell, Edwards and Williamson (1976) have selected the upper acceptable limit of dustfall

(water-insoluble fraction) for residential areas to be 130 mg m^{-2} day^{-1} in their Portland cement dustfall study in Geelong, Victoria. They recommended that "the goal of urban planning authorities should be dustfall no higher than this level in order to guarantee the comfortable enjoyment of life or use of property".

The Department of Public Health of Victoria in 1966 suggested certain typical dustfall figures for various areas (Cantrell, Edwards and Williamson,1976), as shown in Table 5.1, but entrained dust may be lower in Tasmania because of higher soil moisture and greater vegetative cover.

Table 5.1. Typical dustfall figures in various areas.

Classification	Dustfall (water-insoluble solids) (mg m^{-2} day^{-1})
Rural	13 - 65
Residential	40 - 90
Light Industrial	100 - 160
Heavy Industrial	200 - 350

After consideration of many recommendations and suggestions, and based on his dustfall study in Adelaide, Low (1980) proposed that a dustfall figure (water-insoluble components) in excess of 100 mg m^{-2} day^{-1} be considered "slightly dusty". When a figure in excess of 120 mg m^{-2} day^{-1} is found in a residential area, it would be considered "moderately dusty" and likely to draw complaints from the residents. At 140 mg m^{-2} day^{-1}, the area would be regarded as "very dusty" and expected to draw heavy complaints from the residents. These figures, however, could only be used as yardsticks to measure the relative degree of dust pollution in a residential area and by no means should be regarded as 'standard'. For dustfall levels at different places and countries to be comparable, similar dust collectors as well as sampling and analytical methods must be employed, preferably for similar settings or topography, emission sources, and meteorological conditions (Low, 1983). The collection efficiency of a deposit gauge could vary with the design of the gauge and climatic conditions (Kafka and Pottinger, 1965). Its limitations as a collection device have been discussed by Low (1980), Williamson and Cantrell (1980), and Noller, Bloom and Arnold (1981).

5.3 Dustfall rates in the Lower Tamar Valley

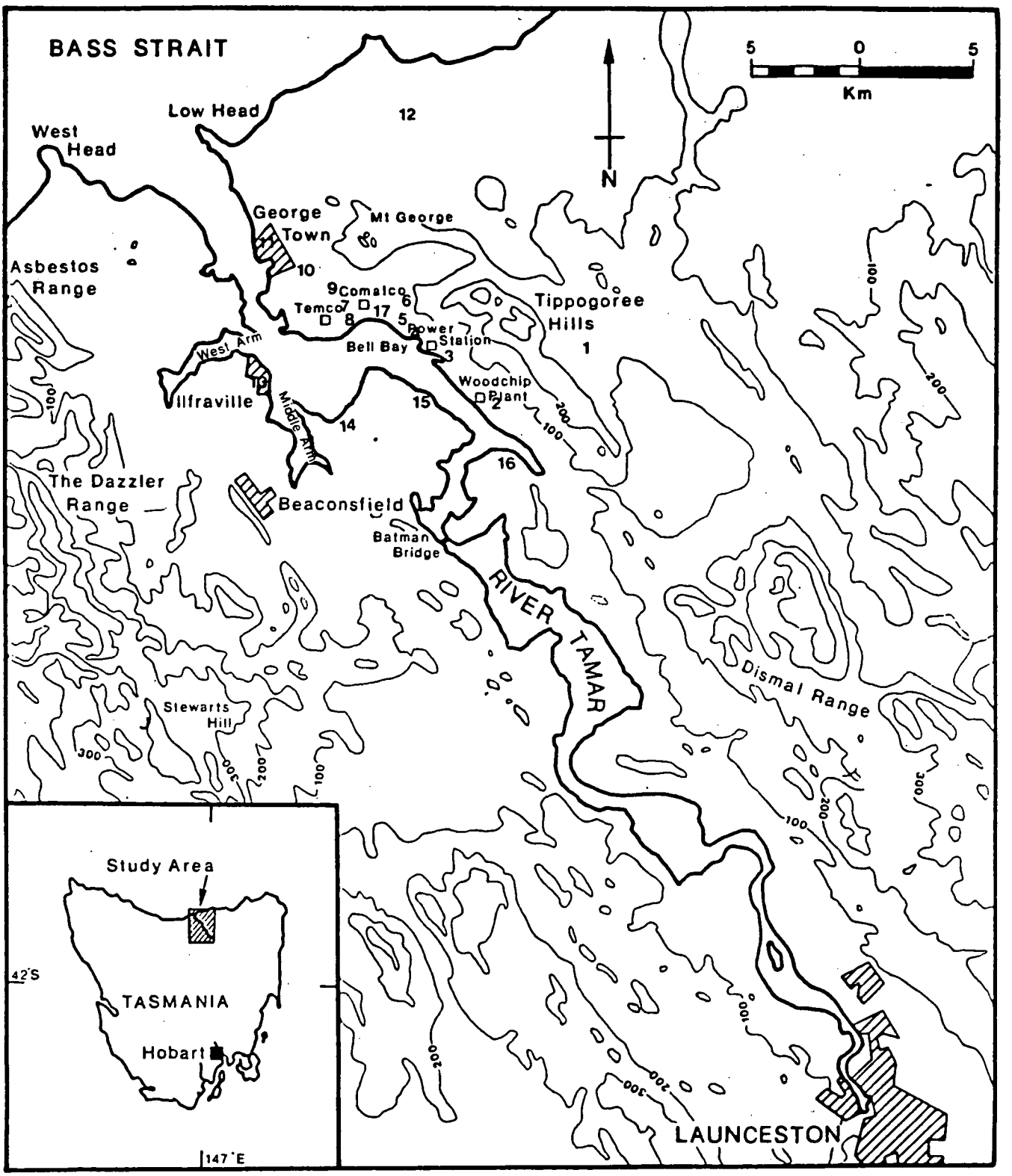
With the introduction of a new potline, Comalco was able to maintain full annual production capacity (117 000 tonnes Al) in 1982-83, even though about 30 old pots were under repair (The Mercury, 1983). However, Temco greatly reduced production (from a full annual capacity of 135 000 tonnes FeMn, 25 000 tonnes SiMn, and 220 000 FeMn sinter to 73 135 tonnes FeMn, 7 530 tonnes SiMn, and 95 073 tonnes FeMn sinter) in the same period due to world economic recession. Hence the results presented below should be viewed in this perspective.

The mean, range, and standard deviation of dustfall rates at each sampling location (Figure 5.1) are given in Table 5.2. The values for locations 1 to 16 were measured from September 1982 to August 1983, while those for location 17 were measured from January to August 1983, and duplicated samples at locations 5, 8, 9, 12 and 17 were measured from February to August 1983.

Table 5.2. Mean Dustfall Rates (mg m^{-2} day^{-1}) in the lower Tamar Valley, September 1982 - August 1983. Samples at location 17 were collected from January to August 1983, while all duplicated samples were collected from February to August 1983.

Site	Mean	Range	Standard Deviation
1	39.1	4.5 - 178.3	56.6
2	39.4	7.3 - 107.8	35.4
3	33.5	10.2 - 177.6	46.6
4	41.5	15.2 - 121.5	35.2
5	80.2	26.4 - 245.6	60.3
5B	42.7	19.2 - 71.4	18.0
6	39.1	8.3 - 89.6	27.4
7	338.3	150.3 - 586.4	156.1
8	117.7	40.2 - 247.0	67.9
8B	93.4	30.8 - 192.1	56.9
9	118.4	62.2 - 193.0	42.9
9B	118.4	57.4 - 319.5	95.2
10	38.1	11.3 - 102.7	33.5
11	52.6	15.1 - 150.3	46.1
12	36.9	1.5 - 129.0	38.4
12B	13.7	5.8 - 32.6	12.7
13	61.1	15.1 - 176.5	47.2
14	32.4	4.3 - 96.2	30.8
15	39.4	6.2 - 115.0	36.7
16	35.3	9.0 - 170.7	44.3
17	73.5	38.0 - 96.9	17.6
17B	108.8	55.2 - 211.9	57.8
17C	90.6	62.6 - 169.7	36.0
17D	86.1	61.3 - 178.1	61.8

Figure 5.1. Locations of deposit gauges for this study (1-17).



All deposit gauges were made of glass containers and funnels except those labelled with "B" at locations 5, 8, 9, and 12, and "C" and "D" at location 17, which were duplicates but with plastic containers and funnels. Of all glass deposit gauges, only 17 and 17B were duplicates.

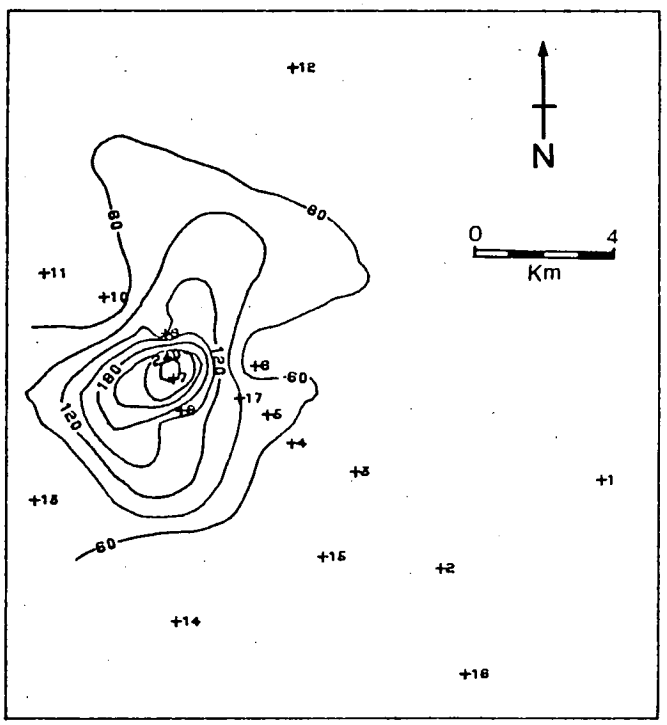
The annual mean dustfall rates in the lower Tamar Valley ranged from 32.4 to 338.3 mg m^{-2} day^{-1}, with standard deviations ranging from 12.7 to 156.1 mg m^{-2} day^{-1}. Only locations 7, 8, 9 and 17, all of which were within 2 km from either Comalco or Temco or both, had annual mean dustfall rates higher than 100 mg m^{-2} day^{-1}. George Town (location 11) had an annual mean dustfall rate of about 53 mg m^{-2} day^{-1}, while the annual mean dustfall rate at Ilfraville (location 13) was slightly higher at 61.1 mg m^{-2} day^{-1}. Location 5, which was about 3 km SE from Comalco, and frequently subjected to the NW prevailing wind, recorded an annual mean dustfall rate of 80 mg m^{-2} day^{-1}.

The dust fallout distribution is best represented by contours drawn by a Zeta 1453 drum plotter using the Surface II graphic system (Figure 5.2). The duplicated samples obtained by plastic deposit gauges were omitted from the plotting for consistency, and the value used for location 17 is an average of 17 and 17B. A similar procedure is also applied for the distribution contours of all trace elements later.

The dustfall levels were generally much higher within 3 km of the Bell Bay industrial area (the centre of which was taken somewhere between Comalco and Temco) than areas further away. However, the patterns of distribution do not seem to quite reflect the frequently occurred NW and SE winds, though the influences of the NE and SW winds, which flowed or channelled through the saddle between Mt George and the Tippogoree Hills, on the dust fallout from the industrial area appear to be more significant. The dust fallout appears to be more spread out in the S to SE direction (with reference to the industrial area), possibly due to the stronger NW prevailing winds. Higher dustfall levels were observed in the SW of the industrial area compared with the NE of the industrial area, possibly due to the more frequent occurrence of NE winds than SW winds (the ratio of maximum percentage occurrence at Station 3 was 2.6 to 1 from December 1982 to November 1983, as shown in Figures 4.43 and 4.44). The relatively high mean dustfall rate at location 13 (61.1 mg m^{-2} day^{-1}), about 5 km SW of Comalco, could be partly

contributed by traffic. The low mean dustfall rate (39 mg m^{-2} day^{-1}) at location 6, about 1 km NE of Comalco, appears to be largely due to the vegetation fence which effectively forms a screen along the highway close to the smelter.

Figure 5.2. Spatial variations of the dustfall rates (mg m^{-2} day^{-1}) at the 17 sampling locations in the lower Tamar Valley. Contour step size = 30 mg $m^{-2}day^{-1}$.



Of the five locations duplicated with plastic deposit gauges, three (locations 5, 8, and 12) show 21% to 63% higher mean dustfall rates in glass deposit gauges than plastic deposit gauges, one (location 9) gives similar results for both types of deposit gauges, and one (location 17) shows slightly higher mean dustfall rates in plastic deposit gauges (Table 5.2). It has been shown that the collection efficiencies of different types of deposit gauges vary, and the values obtained may differ by as much as 50% to 100% (Fisher, 1957), or even as high as 140% (Sanderson, Bradt and Katz, 1963). The difference of the mean dustfall rates between the two duplicated glass deposit gauges (17 and 17B) was 48%. This illustrates the complexity of the atmospheric transport processes.

As a comparison, the annual dustfall rates as monitored by the Tasmanian Department of the Environment in the lower Tamar Valley since 1973 are given in Table 5.3.

The annual mean dustfall rates at the HEC substation were consistently higher than those at other locations since 1976-77. They exceeded 100 mg m^{-2} day^{-1} for most of the years, and the highest recorded was 185 mg m^{-2} day^{-1}, which occurred in 1982-83. It is noted that the HEC substation was situated about half way between locations 5 and 17 of this study. However, the dustfall rate as monitored by the Department of the Environment at this location in 1982-83 was much higher than that at location 17 of this study, even though location 17 was nearer to Comalco. However, the annual mean dustfall rate at Anne Street in 1982-83 as monitored by the Department of the Environment was about the same as that at location 11 of this study. These two sampling locations were less than 200 m from each other.

Table 5.3 Dust fallout in lower Tamar Valley as monitored by the Department of the Environment, 1973-1983. All years ended at June.

(mg m^{-2} day^{-1})

Site	1973-74	74-75	75-76	76-77	77-78	78-79	79-80	80-81	81-82	82-83
Kayena	102	54	49	77	76	74	53	42	35	23
Anne St.	77	51	98	65	45	47	61	47	50	60
HEC Station	86	96	81	132	111	113	122	89	118	185
Reservoir	21	16	16	27	16	21	18	14	16	15

(Source: Department of the Environment, Annual Reports 1973-74 to 1982-83)

Although similar deposit gauges were used, the dustfall rates as obtained by this study and those obtained by the Department of the Environment may not be entirely comparable for the following reasons:

(1) The annual mean dustfall rates for this study were calculated from September 1982 to August 1983, while those for the Department of the Environment were calculated from July 1982 to June 1983.

(2) The deposit gauges of the Department of the Environment were placed at a height of about 1.5 m as compared with 3 m in this study. Hence dust from the ground is more likely to be blown into the gauges if

strong winds prevail.

(3) At least two of the deposit gauges (i.e. those at Kayena and Anne Street) established by the Department of the Environment were found to be sheltered by trees, thus the results were doubtful as being representative of the real deposition situation.

Nevertheless, the ten year records as shown in Table 5.3 were still useful as a guide to the general dust fallout situation in the lower Tamar Valley, even though four sampling locations can hardly be considered adequate to cover the whole area.

5.4 Trace Metals in the Atmospheric Deposition Samples

The atmospheric deposition samples collected in deposit gauges are likely to be contributed by many sources, depending on the meteorological factors as well as the actual siting of the sampling location. A poorly sited deposit gauge such as one on the lower slope of a hill would inevitably catch some dust from the upper slope if wind blows down the hill. Additionally, the possibility of long range transport of pollutants from places hundreds or even thousands of kilometres away cannot be ruled out. For example, dust from Mallee in Victoria was found in the study area during a severe dust storm in February 1983. In spite of all these complications, long term records (say over a period of five years) of dust fallout could give a good indication of the degree of dust pollution in an area.

It is possible to identify the sources of air pollution by analysing the chemical composition of the atmospheric deposition samples using various recommended analytical techniques, as described in Noller, Bloom, and Arnold (1981). Ayling and Bloom (1976) were the first to analyse the heavy metals in dust fallout samples in Hobart so that their sources could be identified and their distributions characterised. The chemical analyses of the atmospheric deposition samples should be regarded as an intergral part of the whole monitoring programme. Without these analyses, the significance of the monitoring programme would be greatly reduced.

Tables 5.4 to 5.16 give the annual mean deposition rates (or fluxes) of Al, F, Mn (insoluble and soluble), Fe, Zn (insoluble and soluble), Cu, Ni, Cr, Co, Cd, and Pb, expressed as $\mu g\ m^{-2}\ day^{-1}$, at each sampling

location as measured from September 1982 to August 1983, except that data for Co, Cd, and Pb are unavailable from November 1982 to January 1983. Of various trace metals, only Mn and Zn were found to have significant soluble concentrations in the filtrate of the samples. Thus, all concentrations measured were for insoluble trace metals unless otherwise specified. However, for trace element F, only the soluble concentrations of the samples were measured.

5.4.1 Deposition Rates of Al, F, Mn, and Fe

Among the various trace elements analysed, Al, F, Mn, and Fe are regarded as the most important in this study. These four elements, though commonly found in soils and sea-sprays, are used as elemental tracers of the air emissions from the two heavy industries (Al and F from Comalco, Mn and Fe from Temco). By comparing the deposition rates of these elements at various locations with that of location 12, the intended 'background' location, it is possible to identify their sources of emissions.

Table 5.4. Mean deposition rates of Al ($\mu g\ m^{-2}\ day^{-1}$) in the lower Tamar Valley, September 1982 - August 1983.

Site	Mean	Range	Standard Deviation	% of Composition
1	650.0	94.2 - 4808.8	1382.5	1.70
2	1110.3	195.5 - 4694.5	1377.3	2.80
3	1178.6	319.2 - 6934.8	1858.4	3.50
4	1246.5	313.0 - 4491.3	1132.8	3.00
5	2463.7	1046.9 - 4788.2	1365.3	3.07
5B	2221.9	1166.5 - 3627.9	841.9	5.20
6	1153.3	340.5 - 3909.4	984.2	2.95
7	2887.8	772.9 - 6305.5	1932.9	0.85
8	2741.5	1264.9 - 9051.9	2318.4	2.33
8B	9360.2	1300.0 -24400.0	8634.5	10.02
9	2949.1	473.3 - 6670.0	2284.6	2.49
9B	2949.6	1842.2 - 3825.9	806.0	2.49
10	1087.6	212.5 - 3191.1	889.3	2.85
11	1221.7	278.5 - 5480.8	1526.4	2.32
12	445.2	33.1 - 1628.3	581.0	1.21
12B	397.1	108.5 - 1154.3	505.4	2.90
13	1044.0	178.3 - 5674.0	1516.0	1.71
14	531.9	90.5 - 2794.6	786.1	1.64
15	859.7	201.2 - 3898.0	1002.9	2.18
16	849.9	148.4 - 4723.6	1257.3	2.41
17	3668.6	1619.0 - 7034.1	1732.4	4.99
17B	7608.9	3900.0 -13800.0	4405.2	6.99
17C	5662.7	3346.3 - 8339.4	2037.9	6.25
17D	6116.6	4830.0 -12020.0	3894.3	7.10

Table 5.5. Mean deposition rates of soluble F ($\mu g\ m^{-2}\ day^{-1}$) in the lower Tamar Valley, September 1982 - August 1983.

Site	Mean	Range	Standard Deviation	% of Composition
1	293.7	103.4 - 1104.6	292.9	0.75
2	471.0	256.2 - 744.8	164.5	1.20
3	581.5	280.9 - 1398.3	291.4	1.74
4	1051.5	481.8 - 2907.5	619.2	2.53
5	2528.9	1302.2 - 7379.1	1819.1	3.15
5B	2695.7	413.8 - 4112.6	1474.1	6.31
6	727.0	91.9 - 2649.8	668.5	1.86
7	943.1	292.7 - 1876.5	491.2	0.28
8	2221.6	760.6 - 9496.2	2680.4	1.89
8B	2217.8	787.5 - 4947.5	1649.0	2.37
9	1901.7	243.3 - 4487.5	1558.5	1.61
9B	2330.3	345.2 - 4829.3	1622.3	1.97
10	441.3	104.1 - 743.2	213.4	1.16
11	279.9	51.7 - 684.8	181.1	0.53
12	89.9	7.2 - 182.2	59.0	0.24
12B	90.2	65.0 - 113.7	24.4	0.66
13	244.8	96.4 - 720.7	163.9	0.40
14	155.3	54.4 - 253.0	70.6	0.48
15	312.9	202.7 - 378.1	54.6	0.79
16	872.4	216.5 - 4859.3	1282.1	2.47
17	11779.5	2961.5 - 58543.7	17707.7	16.03
17B	13356.3	2820.0 - 26630.0	9781.5	12.28
17C	7670.5	502.3 - 4980.1	4635.7	8.47
17D	12369.2	3920.0 - 31960.0	10962.9	14.37

Table 5.6. Mean deposition rates of Mn ($\mu g\ m^{-2}\ day^{-1}$) in the lower Tamar Valley, September 1982 - August 1983.

Site	Mean	Range	Standard Deviation	% of Composition
1	23.3	9.0 - 50.6	13.3	0.06
2	108.2	24.7 - 304.9	95.4	0.27
3	121.4	20.8 - 292.1	75.6	0.36
4	128.3	37.2 - 257.8	66.7	0.31
5	298.9	33.7 - 801.4	199.0	0.37
5B	176.7	34.3 - 350.6	95.9	0.41
6	101.8	31.0 - 179.4	48.5	0.26
7	895.3	302.7 - 1709.8	429.2	0.26
8	2113.9	701.9 - 5744.9	1533.5	1.80
8B	1855.0	498.2 - 4057.6	1428.1	1.99
9	447.0	153.2 - 869.9	265.5	0.38
9B	510.0	125.0 - 1749.7	569.0	0.43
10	363.8	72.6 - 619.4	161.9	0.95
11	878.4	207.6 - 1855.2	492.8	1.67
12	23.8	8.0 - 62.3	16.4	0.06
12B	17.7	5.3 - 28.9	9.8	0.13
13	137.3	29.4 - 298.4	72.2	0.22
14	28.5	11.9 - 54.7	14.1	0.09
15	238.7	101.1 - 543.4	136.0	0.61
16	47.6	15.2 - 93.4	22.8	0.13
17	182.8	102.0 - 295.0	66.6	0.25
17B	409.4	55.0 - 675.1	223.7	0.38
17C	222.9	58.2 - 441.6	146.9	0.25
17D	306.0	221.2 - 449.7	83.7	0.36

Table 5.7. Mean deposition rates of soluble Mn ($\mu g\ m^{-2}\ day^{-1}$) in the lower Tamar Valley, September 1982 - August 1983.

Site	Mean	Range	Standard Deviation	% of Composition
1	42.9	19.5 - 141.5	38.1	0.11
2	106.5	39.8 - 195.5	63.1	0.27
3	129.2	4.3 - 201.6	64.4	0.39
4	154.5	1.3 - 250.3	72.2	0.37
5	124.3	3.8 - 300.5	112.1	0.15
5B	139.3	10.0 - 277.8	107.5	0.33
6	83.6	16.9 - 232.5	76.9	0.21
7	436.1	11.9 -1655.6	535.1	0.13
8	1562.2	5.1 -7408.8	2300.1	1.33
8B	863.7	25.9 -1996.9	912.6	0.92
9	121.6	7.9 - 426.7	156.1	0.10
9B	182.3	10.9 - 505.2	214.7	0.15
10	153.6	1.1 - 490.6	157.9	0.40
11	323.3	30.6 - 998.2	384.9	0.61
12	13.8	2.1 - 35.6	13.8	0.04
12B	39.4	13.1 - 71.4	29.2	0.29
13	32.0	5.4 - 134.4	39.3	0.05
14	53.1	15.9 - 87.2	29.8	0.16
15	150.3	3.7 - 328.0	112.0	0.38
16	122.5	14.0 - 234.1	72.4	0.35
17	177.1	36.9 - 436.6	129.1	0.24
17B	222.7	78.0 - 561.8	202.0	0.20
17C	194.7	10.1 - 475.4	154.8	0.21
17D	329.5	7.0 - 663.8	256.9	0.38

Table 5.8. Mean deposition rates of Fe ($\mu g\ m^{-2}\ day^{-1}$) in the lower Tamar Valley, September 1982 - August 1983.

Site	Mean	Range	Standard Deviation	% of Composition
1	684.6	103.6 - 5493.1	1597.8	1.75
2	1102.7	206.7 - 4061.7	1353.6	2.80
3	906.2	170.2 - 5716.0	1552.3	2.71
4	895.2	123.6 - 4237.4	1119.0	2.16
5	1166.6	390.1 - 2811.9	855.2	1.45
5B	723.4	125.4 - 1769.3	580.9	1.69
6	733.7	103.5 - 2782.6	744.9	1.88
7	1318.8	386.5 - 3316.2	782.2	0.39
8	1562.4	497.9 - 4383.0	1081.2	1.33
8B	1531.3	143.9 - 2829.7	897.0	1.64
9	1158.4	44.2 - 3624.2	1188.1	0.98
9B	1109.9	54.2 - 1810.3	694.1	0.94
10	683.1	81.7 - 2853.2	800.8	1.79
11	1335.0	437.6 - 5115.4	1353.5	2.54
12	393.2	85.4 - 1537.9	474.3	1.07
12B	360.5	108.5 - 939.9	392.2	2.63
13	1197.8	267.5 - 5484.9	1436.1	1.96
14	574.5	19.9 - 2303.9	730.6	1.77
15	595.7	78.0 - 3197.9	842.0	1.51
16	812.4	125.8 - 5216.5	1409.3	0.69
17	1173.8	570.7 - 2216.6	525.2	1.60
17B	1899.6	677.2 - 4154.7	1243.6	1.75
17C	1249.8	620.6 - 1685.6	490.8	1.38
17D	1014.8	836.5 - 1511.1	547.0	1.18

Table 5.9. Mean deposition rates of Zn ($\mu g\ m^{-2}\ day^{-1}$) in the lower Tamar Valley, September 1982 - August 1983.

Site	Mean	Range	Standard Deviation	% of Composition
1	25.6	0.7 - 212.7	62.6	<0.01
2	29.1	1.5 - 143.3	39.9	0.07
3	12.6	2.1 - 54.6	14.6	0.04
4	12.4	2.1 - 33.2	9.7	0.03
5	44.7	9.5 - 26.4	41.6	0.06
5B	14.8	5.4 - 45.3	14.0	0.03
6	19.4	2.6 - 110.4	29.8	0.05
7	546.8	252.2 - 1240.1	364.0	0.16
8	73.8	12.7 - 351.6	102.2	0.06
8B	30.6	12.6 - 97.3	33.3	0.03
9	397.7	38.4 - 1348.5	381.4	0.34
9B	19.1	13.4 - 29.4	6.2	0.02
10	42.0	3.7 - 251.2	72.8	0.11
11	184.2	7.8 - 890.6	267.6	0.35
12	39.1	0.3 - 117.7	41.4	0.11
12B	11.0	2.8 - 29.8	12.6	0.08
13	161.2	5.3 - 976.3	270.0	0.26
14	19.8	1.4 - 70.7	23.9	0.06
15	21.4	2.0 - 105.3	28.5	<0.01
16	64.3	8.5 - 343.1	104.3	0.18
17	71.5	7.7 - 253.3	75.6	0.10
17B	267.4	11.2 - 705.4	262.5	0.25
17C	29.8	11.5 - 51.1	14.5	0.03
17D	45.8	11.3 - 138.5	47.4	0.53

Table 5.10. Mean deposition rates of soluble Zn ($\mu g\ m^{-2}\ day^{-1}$) in the lower Tamar Valley, September 1982 - August 1983.

Site	Mean	Range	Standard Deviation	% of Composition
1	47.6	7.3 - 226.4	71.1	0.12
2	507.2	2.0 - 2318.5	833.1	1.29
3	169.3	17.7 - 638.5	199.8	0.51
4	127.7	17.2 - 548.1	150.8	0.31
5	44.5	6.5 - 155.2	46.0	0.06
5B	74.8	16.9 - 188.3	75.5	0.18
6	88.7	13.8 - 355.7	135.6	0.23
7	488.3	55.2 - 907.0	277.6	0.14
8	172.2	5.1 - 901.5	295.0	0.15
8B	29.4	5.7 - 86.0	43.3	0.03
9	882.3	1.9 - 2732.3	753.2	0.77
9B	58.6	16.1 - 162.4	58.3	0.05
10	392.2	7.4 - 2238.1	701.9	1.03
11	707.1	15.3 - 1632.5	499.2	1.34
12	93.4	11.6 - 683.2	211.0	0.25
12B	614.3	426.4 - 1106.7	329.2	4.48
13	380.8	14.7 - 1079.9	367.1	0.62
14	168.3	7.0 - 1242.0	406.4	0.51
15	32.7	3.0 - 184.0	52.8	0.08
16	802.2	10.5 - 2778.0	981.1	2.27
17	818.6	9.7 - 2152.8	1008.7	1.11
17B	1209.3	443.3 - 2696.4	1052.2	1.11
17C	134.8	2.9 - 228.9	83.2	0.15
17D	92.1	4.2 - 161.5	67.1	0.11

Table 5.11. Mean deposition rates of Cu ($\mu g\ m^{-2}\ day^{-1}$) in the lower Tamar Valley, September 1982 - August 1983.

Site	Mean	Range	Standard Deviation	% of Composition
1	3.7	0.5 - 30.0	8.7	0.01
2	4.9	3.0 - 10.1	2.2	0.01
3	3.5	1.7 - 9.2	2.1	0.01
4	4.2	1.4 - 9.1	2.3	0.01
5	7.6	3.9 - 17.5	4.1	0.01
5B	5.5	2.9 - 7.9	1.9	0.01
6	3.9	1.4 - 10.8	2.6	0.01
7	17.6	5.3 - 35.1	10.8	<0.01
8	8.0	0.9 - 13.7	4.0	<0.01
8B	9.8	4.0 - 21.5	6.6	0.01
9	8.5	1.6 - 18.9	6.2	<0.01
9B	8.3	2.5 - 14.4	5.1	<0.01
10	2.2	0.7 - 3.7	0.9	<0.01
11	4.6	1.2 - 9.0	2.5	<0.01
12	1.7	0.7 - 2.9	0.7	<0.01
12B	1.7	1.3 - 3.0	0.8	0.01
13	4.0	2.2 - 11.3	2.5	<0.01
14	2.5	0.8 - 8.6	2.4	<0.01
15	2.4	1.2 - 3.7	0.7	<0.01
16	4.0	0.7 - 18.3	4.8	0.01
17	11.3	7.1 - 19.5	3.9	0.15
17B	17.3	7.8 - 36.7	11.1	0.02
17C	20.8	10.4 - 37.6	11.4	0.02
17D	18.7	8.9 - 25.9	7.8	0.02

Table 5.12. Mean deposition rates of Ni ($\mu g\ m^{-2}\ day^{-1}$) in the lower Tamar Valley, September 1982 - August 1983.

Site	Mean	Range	Standard Deviation	% of Composition
1	1.1	0.2 - 2.7	0.9	<0.01
2	3.5	1.1 - 11.0	2.5	<0.01
3	7.6	1.3 - 21.6	6.1	0.02
4	17.2	5.3 - 85.3	22.0	0.04
5	33.1	14.7 - 68.8	21.3	0.04
5B	30.8	10.4 - 69.4	26.1	0.07
6	8.1	2.3 - 20.8	4.9	0.02
7	7.3	3.5 - 17.0	3.7	<0.01
8	11.7	4.7 - 24.8	6.3	0.01
8B	30.5	4.8 - 32.2	32.2	0.03
9	17.2	2.6 - 60.4	16.3	0.01
9B	17.5	8.5 - 42.7	12.2	0.01
10	2.9	0.3 - 6.7	1.7	<0.01
11	2.4	0.6 - 4.1	1.2	<0.01
12	0.5	0.3 - 1.4	0.5	<0.01
12B	0.1	0.3 - 0.3	0.2	<0.01
13	1.7	0.5 - 5.3	1.5	<0.01
14	0.9	0.2 - 2.4	0.9	<0.01
15	2.8	1.0 - 6.7	1.7	<0.01
16	2.4	0.2 - 5.6	1.5	<0.01
17	74.7	35.1 - 149.0	44.4	<0.01
17B	148.3	76.4 - 315.9	99.3	0.14
17C	87.4	35.0 - 149.4	49.2	0.10
17D	120.4	75.7 - 212.6	48.7	0.14

Table 5.13. Mean deposition rates of Cr ($\mu g\ m^{-2}\ day^{-1}$) in the lower Tamar Valley, September 1982 - August 1983.

Site	Mean	Range	Standard Deviation	% of Composition
1	7.2	0.2 - 21.3	12.2	0.02
2	0.7	0.2 - 1.2	0.5	<0.01
3	0.9	0.2 - 2.3	1.0	<0.01
4	0.6	0.2 - 1.8	0.6	<0.01
5	0.9	0.2 - 2.6	1.0	<0.01
5B	0.3	0.2 - 0.7	0.2	<0.01
6	0.7	0.6 - 0.7	0.04	<0.01
7	1.3	0.2 - 3.0	1.0	<0.01
8	0.6	0.2 - 1.3	0.3	<0.01
8B	0.2	0.2 - 0.4	0.1	<0.01
9	0.8	0.2 - 3.9	1.3	<0.01
9B	0.5	0.2 - 0.9	0.3	<0.01
10	0.5	0.2 - 0.9	0.3	<0.01
11	1.1	0.2 - 2.1	0.7	<0.01
12	0.2	0.2 - 0.5	0.1	<0.01
12B	0.3	0.3 - 0.3	0.3	<0.01
13	1.6	0.4 - 3.3	1.1	<0.01
14	0.8	0.2 - 1.9	0.9	<0.01
15	0.4	0.2 - 0.8	0.2	<0.01
16	5.0	0.2 - 23.4	10.3	0.01
17	1.1	0.2 - 2.2	0.7	<0.01
17B	2.3	0.5 - 6.1	2.2	<0.01
17C	0.9	0.4 - 2.4	0.8	<0.01
17D	1.1	0.6 - 2.8	0.8	<0.01

Table 5.14. Mean deposition rates of Co ($\mu g\ m^{-2}\ day^{-1}$) in thelower Tamar Valley, September 1982 - August 1983. (excluding November 1982 - January 1983).

Site	Mean	Range	Standard Deviation	% of Composition
1	0.1	0.2 - 0.4	0.1	<0.01
2	0.9	0.2 - 3.5	1.1	<0.01
3	0.5	0.2 - 1.7	0.6	<0.01
4	0.6	0.2 - 1.7	0.5	<0.01
5	1.2	0.5 - 2.2	0.5	<0.01
5B	1.0	0.6 - 2.1	0.6	<0.01
6	0.6	0.2 - 1.1	0.3	<0.01
7	1.2	0.6 - 2.3	0.5	<0.01
8	1.5	0.8 - 3.1	0.9	<0.01
8B	1.7	1.1 - 2.7	0.6	<0.01
9	1.3	0.8 - 1.8	0.4	<0.01
9B	1.1	0.4 - 2.3	0.6	<0.01
10	0.6	0.5 - 1.2	0.3	<0.01
11	0.7	0.4 - 2.2	0.6	<0.01
12	0.3	0.2 - 0.8	0.3	<0.01
12B	0.3	0.2 - 0.7	0.2	<0.01
13	1.2	0.2 - 5.3	1.6	<0.01
14	0.3	0.2 - 1.3	0.4	<0.01
15	0.4	0.4 - 1.0	0.3	<0.01
16	0.5	0.2 - 1.1	0.4	<0.01
17	2.3	1.5 - 3.6	0.8	<0.01
17B	3.8	1.8 - 6.7	1.8	<0.01
17C	2.6	1.6 - 3.8	1.0	<0.01
17D	2.5	2.0 - 4.4	1.4	<0.01

Table 5.15. Mean deposition rates of Cd ($\mu g\ m^{-2}\ day^{-1}$) in the lower Tamar Valley, September 1982 - August 1983. (excluding November 1982 - January 1983).

Site	Mean	Range	Standard Deviation	% of Composition
1	0.9	0.03 - 5.7	2.0	<0.01
2	0.6	0.1 - 2.2	0.7	<0.01
3	0.8	0.2 - 2.2	0.7	<0.01
4	0.4	0.04 - 1.7	0.5	<0.01
5	0.3	0.03 - 0.5	0.2	<0.01
5B	0.5	0.2 - 1.2	0.3	<0.01
6	0.3	0.2 - 0.4	0.1	<0.01
7	1.1	0.6 - 2.2	0.6	<0.01
8	0.3	0.1 - 0.6	0.2	<0.01
8B	0.6	0.2 - 1.5	0.5	<0.01
9	0.7	0.5 - 1.3	0.3	<0.01
9B	0.5	0.2 - 0.9	0.3	<0.01
10	0.3	0.1 - 0.7	0.2	<0.01
11	1.3	0.4 - 3.4	1.1	<0.01
12	0.4	0.1 - 1.3	0.4	<0.01
12B	0.3	0.2 - 0.4	0.1	<0.01
13	0.7	0.2 - 3.0	0.9	<0.01
14	0.3	0.2 - 0.4	0.1	<0.01
15	0.3	0.2 - 0.4	0.1	<0.01
16	2.5	0.1 - 6.1	2.3	0.01
17	0.5	0.2 - 1.5	0.5	<0.01
17B	0.5	0.2 - 0.7	0.2	<0.01
17C	0.7	0.3 - 0.9	0.2	<0.01
17D	1.0	0.4 - 1.9	0.7	<0.01

Table 5.16. Mean deposition rates of Pb ($\mu g\ m^{-2}\ day^{-1}$) in the lower Tamar Valley, September 1982 - August 1983. (excluding November 1982 - January 1983).

Site	Mean	Range	Standard Deviation	% of Composition
1	4.1	0.8 - 34.4	10.1	0.01
2	2.9	0.4 - 9.0	3.6	<0.01
3	6.0	4.3 - 26.1	8.1	0.02
4	8.9	3.5 - 27.8	10.1	0.02
5	4.5	0.9 - 11.5	4.0	<0.01
5B	10.1	0.4 - 20.1	8.1	0.02
6	3.5	0.6 - 9.3	3.2	<0.01
7	4.4	0.2 - 10.0	4.5	0.01
8	4.1	1.1 - 14.6	5.1	<0.01
8B	5.2	1.1 - 10.3	4.4	<0.01
9	7.2	0.8 - 36.6	11.8	<0.01
9B	6.7	1.7 - 12.4	4.0	<0.01
10	7.7	0.3 - 45.8	14.2	0.02
11	6.0	0.6 - 14.1	6.1	0.01
12	2.8	0.2 - 15.0	4.8	<0.01
12B	1.0	0.4 - 1.6	0.9	<0.01
13	18.9	0.2 - 13.3	4.2	<0.01
14	2.0	0.2 - 84.0	28.9	0.03
15	2.0	1.1 - 5.2	2.0	<0.01
16	5.9	0.4 - 34.1	11.2	0.02
17	6.6	0.5 - 20.0	8.8	<0.01
17B	6.6	0.5 - 12.4	5.3	<0.01
17C	12.5	4.3 - 32.6	13.9	0.01
17D	15.8	3.0 - 38.7	19.8	0.02

Table 5.17. Annual mean deposition rates of Al, F, Mn(total) and Fe ($\mu g\ m^{-2}\ day^{-1}$) in glass deposit gauges at 17 sampling locations in the lower Tamar Valley, September 1982 - August 1983. The ratios to background levels, and the ratios of Al and F, insoluble (i) and soluble (s) Mn, Fe and Mn(total) are also given in the table.

Site	Trace Elements				Ratio to background levels				Al:F	Mn(i):Mn(s)	Fe:Mn(total)
	Al	F	Mn(total)	Fe	Al	F	Mn(total)	Fe			
1	650.0	293.7	66.2	684.6	1.5	3.3	1.8	1.7	2.2	0.5	10.3
2	1110.3	471.0	214.7	1102.7	2.5	5.2	5.7	2.8	2.4	1.0	5.1
3	1178.6	581.5	250.6	906.2	2.6	6.5	6.7	2.3	2.0	0.9	3.6
4	1246.5	1051.5	282.8	895.2	2.8	11.7	7.5	2.3	1.2	0.8	3.2
5	2463.7	2528.9	423.2	1166.6	5.5	28.1	11.3	3.0	1.0	2.4	2.8
6	1153.3	727.0	185.4	733.7	2.6	8.1	4.9	1.9	1.6	1.2	4.0
7	2887.8	943.1	1331.4	1318.8	6.5	10.5	35.4	3.4	3.1	2.1	1.0
8	2741.5	2221.6	3676.1	1562.4	6.2	24.7	97.8	4.0	1.2	1.4	0.4
9	2949.1	1901.7	568.6	1158.4	6.6	21.2	15.1	2.9	1.6	3.7	2.0
10	1087.6	441.3	537.4	683.1	2.4	4.9	14.3	1.7	2.5	2.4	1.3
11	1221.7	279.9	1201.7	1335.0	2.7	3.1	32.0	3.4	4.4	2.7	1.1
12+	445.2	89.9	37.6	393.2	1.0	1.0	1.0	1.0	5.0	1.7	10.5
13	1044.0	244.8	169.3	1197.8	2.3	2.7	4.5	3.0	4.3	4.3	7.1
14	531.9	155.3	81.6	574.5	1.2	1.7	2.2	1.5	3.4	0.5	7.0
15	859.7	312.9	389.0	595.7	1.9	3.5	10.3	1.5	2.7	1.6	1.5
16	849.9	872.4	170.1	812.4	1.9	9.7	4.5	2.1	1.0	0.4	4.8
17*	5638.8	12567.9	359.9	1536.7	12.7	138.8	13.2	3.9	0.5	1.5	3.1

+ Intended 'background' location.

* Average of duplicated samples collected in deposit gauges 17 and 17B.

For consistency, only the mean deposition rates of the trace elements collected in glass deposit gauges, which form the major part of the monitoring network, are discussed. The mean deposition rate of each trace element at location 17 as discussed below is the average of the mean deposition rates for glass deposit gauges 17 and 17B.

The annual mean deposition rates of Al, F, Mn(total) and Fe in the glass deposit gauges at various sampling locations ranged from 445 to 5 638, 89 to 12 568, 38 to 3 676, and 392 to 1 534 $\mu g\ m^{-2}\ day^{-1}$ respectively (Table 5.17). As no deposition standards for these trace elements are available for comparison, their effects on the local environment and ecosystems are difficult to assess. A deposition rate of 100 $\mu g\ m^{-2}\ day^{-1}$ is adopted by the South Carolina Pollution Control Authority to be the ambient air standard for gaseous F (as HF for a 30 day period) (Rich, 1973). However, this may not be applicable to the lower Tamar Valley unless the figure is derived from similar sampling and analytical techniques. Only at the intended 'background' location that the monthly deposition rates of F were less than 100 $\mu g\ m^{-2}\ day^{-1}$.

Normalising the mean deposition rates to the intended 'background' levels (which happened to be the lowest in all cases), the ratios vary from 1.2 to 12.7 for Al, 1.7 to 139.8 for F, 1.8 to 97.8 for Mn(total), 1.5 to 4.0 for Fe. The background levels of Al and Fe were much higher than those of F and Mn respectively.

While location 17, about 1 km ESE of Comalco had the highest mean deposition rates of Al (5 638 $\mu g\ m^{-2}\ day^{-1}$) and F (12 568 $\mu g\ m^{-2}\ day^{-1}$), location 8, about 1 km E of Temco, recorded the highest mean deposition rates of total Mn (3 676 $\mu g\ m^{-2}\ day^{-1}$) and Fe (1 534 $\mu g\ m^{-2}\ day^{-1}$). In general, the annual mean deposition rates of these four trace elements were much higher closer to their respective emission sources, though the air emissions could at least travel 10 km up the valley from the industrial area, as evidenced by the relatively high deposition rates of F and Mn at location 16 (about 10 and 5 times higher than the intended 'background' levels).

Figures 5.3 and 5.4 show the annual mean deposition rates of Al and F, Mn and Fe as a function of distance along the NW-SE sectors with Comalco and Temco as centres respectively. The gradients were generally much steeper within 3 km of the emission sources, and then decreased

gradually with distance. The deposition patterns of Al and F were similar within 3 km. However, the fluoride level showed an increase after a distance of 7 km SE of Comalco (i.e. from locations 2 to 16). This peculiar phenomenon may have been caused by the gaseous or submicron aerosol fluorides which could be transported by the prevailing NW winds

Figure 5.3. Mean deposition rates of Al and F as a function of distance along the NW-SE sectors from Comalco. The points on the graph refer to the relevant sampling locations.

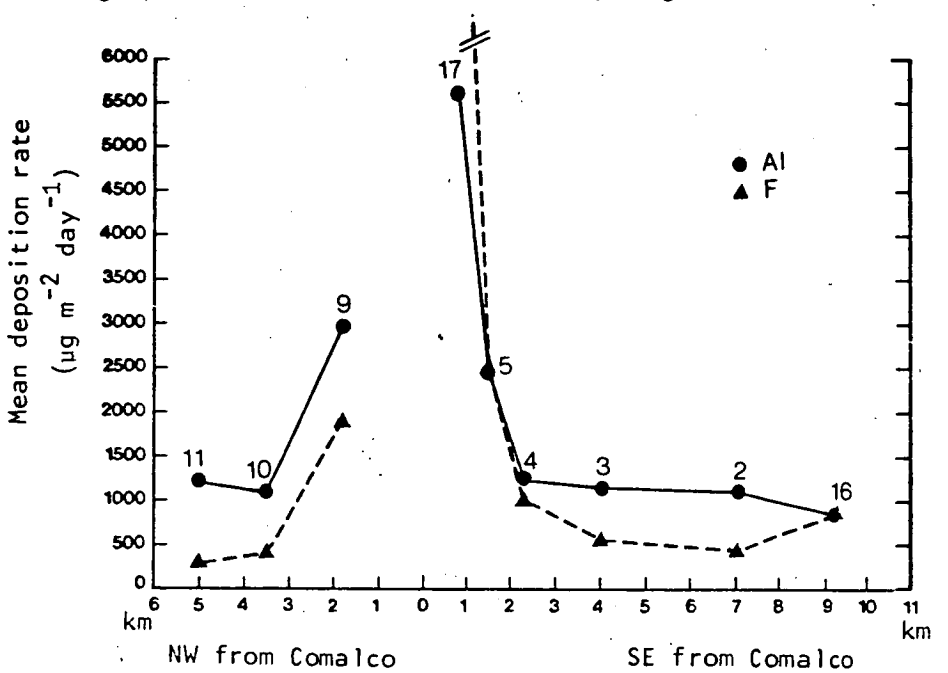
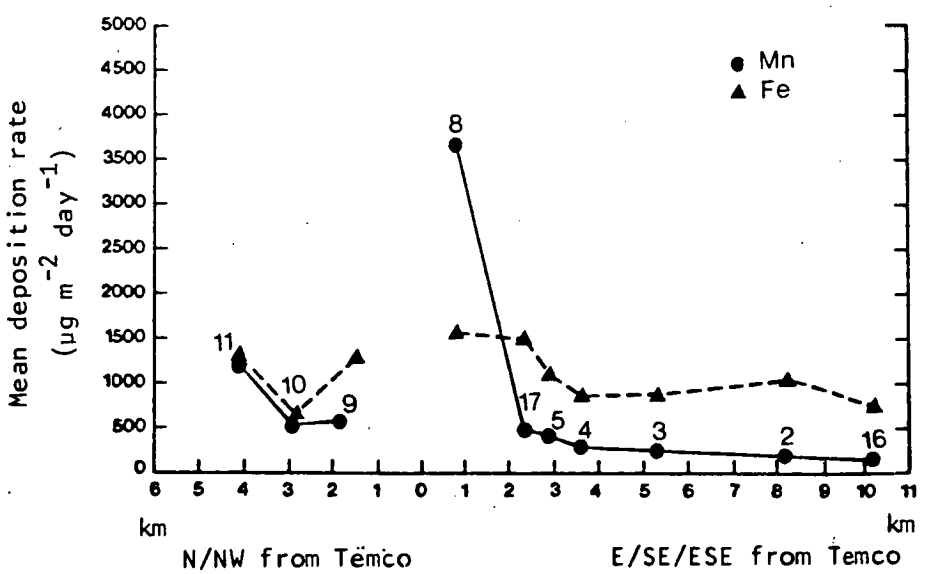


Figure 5.4. Mean deposition rates of Mn(total) and Fe as a function of distance along the NW-SE sectors from Temco. The points on the graph refer to the relevant sampling locations.



further up the valley before rainout or washout. Rainout is the absorption of pollutants into cloud droplets or ice crystals; washout is the absorption of pollutants during precipitation, much as the scrubbing action of a shower (Batterman, Gruhl, and Labys, 1983). The relatively high levels of Fe at locations 17 and 2 were likely to be partially contributed by other local sources as the former was near Comalco, while the latter was close to a rail-line near the woodchip plants. The thermal power station could also be a source of Fe deposition (Fe is contained in the fuel oil as an impurity), particularly at locations 3 and 4. Location 11 had higher mean deposition rates of Al, Mn and Fe than location 10 though it was more distant from the industrial area. These could be locally induced as location 11 was within George Town, hence subject to more traffic and other local emission sources such as household burning than that at location 10 which was in an open field near the foothills of Mt George.

The distributions of Al, F, Mn and Fe from the industrial area appear to extend to the other side of the river, as evidenced by the rather high mean deposition rates of these elements at location 13 (about 2 to 5 times higher than the intended 'background' levels). It was highly likely that these elements could have been transported by the NE winds flowing from the saddle between Mt George and the Tippogoree Hills, particularly from late night to early morning (the frequency of occurrence varying from 26% at 2100 hours to 11% at 600 hours from December 1982 to November 1983). While these winds could be katabatic, which occurs most frequently in colder months, as characterised by their low speeds (generally < 2.0 m s^{-1}) and shallow depth (< 100 m), they could also be due to the channelling of the lower part of the synoptic winds, notably the easterlies in summer, by the saddle (in this case, the wind speeds would be much higher - between 3.4 and 7.9 m s^{-1}). The NE katabatic winds could carry air pollutants in higher concentration, hence be more detrimental to the environment, especially when the winds become moist as they cross over the river during cold, calm and foggy nights or mornings (surface inversions are most likely to develop under these stable conditions). A total of 51 fog days was observed at Bell Bay from September 1982 to August 1983 (see Table 4.15 on page 121). Likewise, the blocking of the lower part of the NE channelled or ambient wind by

the Asbestos/Dazzler Ranges (see Section 4.8.2, page 253) could also result in the accumulation of the air pollutants from the industrial area on the western shore.

Although the annual mean dustfall rate at location 6, located about 1 km NE of Comalco, was only slightly higher than the intended 'background' level (Table 5.2), the annual mean deposition rates of Al, F, Mn(total), and Fe were about 2.5, 8, 5, and 2 times higher than the intended 'background' levels respectively. This illustrates the importance of including the chemical analyses for identifying the emission sources in any atmospheric deposition monitoring. The relatively high deposition rate of F at location 6 shows that this element was more influenced by the SW winds and less affected by the vegetation screen along the highway close to Comalco compared with the trace metals, possibly due to its smaller particle size. Some of the F compounds might appear as gaseous pollutants, hence could be transported at greater height and to further distance by turbulence. Turbulence diffusion controls the transport of submicron particles to the surface, as the effect of sedimentation is negligible (United Nations, 1979).

The ratios of deposition of Al and F vary from 0.5 at location 17 (closest to Comalco) to 5.0 at location 12 (intended 'background' location), while those for Fe and Mn(total) vary from 0.4 at location 8 (closest to Temco) to 10.5 at location 12. In general, the sampling locations close to Comalco and Temco tend to have small values of Al: F (< 2.0), and Fe:Mn(total) (<1.5). Location 16 (9.3 km SE of Comalco) had a similar ratio of Al and F (1.0) as location 5 (1.5 km SE of Comalco). This further suggests that the air emissions from Comalco could at least travel up to 9 km downwind of the source.

The ratio of insoluble to soluble Mn at each sampling location was also determined. Higher ratios (> 2.0) were found near to Temco. This implies that the coarser Mn particles which settled near the source were less soluble than those airborne submicron particles or aerosols, which have longer residence times and could be transported much further away. Typical residence times for aerosols (< 1 μm) were found to be 4-7 days by Davis and Galloway (1981). Muller (1982) and Rohbock (1982) found that washout is the process which predominantly removes coarse particles of the lower air layers.

The high standard deviations of the deposition rates of the trace elements at most locations reflect the wide ranges of deposition rates throughout the year (Tables 5.4 to 5.7). This is to be expected as the deposition rate is a function of many factors including the emission strength (this is influenced by the rate of production and air pollution control strategy), and meteorological conditions, hence it can not be uniform in space and in time.

The percentage compositions of Al, F, Mn(total) and Fe in the deposition samples vary from location to location (Tables 5.4 to 5.7). The ranges are 1%-10% for Al, 0.2%-16% for F, 0.06%-2% for insoluble Mn, 0.04%-1.3% for soluble Mn, and 0.4%-2.8% for Fe. Most locations close to the two heavy industries received higher percentage compositions of the trace elements than those at remote areas, with the exception of Fe, which appears to be strongly influenced by other local sources.

The spatial variations of Al, F, Mn(total) and Fe are best illustrated in Figures 5.5 to 5.8, which were drawn by the Zeta 1450 drum plotter using the Surface II graphic system (Sampson, 1978). The distribution patterns of Al and F were very similar, particularly in areas within 5 km from Comalco, suggesting that there is a strong correlation between these two elements. However, the distribution patterns for Mn(total) and Fe varied, possibly due to the influence of other local sources on Fe. In general, the distributions of these elements appear to reflect, to some extent, the major wind flows (NW and SE winds, NE and SW winds) experienced in the industrial area.

The different features of the distribution between each element were probably due to the different locality of the emission sources and the different particle size distribution with respect to the meteorological conditions, especially the wind vectors. For example, the SW distribution patterns are more evident for Al and F than Mn and Fe because Comalco is closer to the saddle between Mt George and the Tippogorce Hills than Temco, hence it is more in the pathway of the NE winds flowing down the saddle. Due to the lack of sampling locations between locations 1 and 12 (this happens to be hilly areas), the extrapolated deposition contours in the areas, as drawn by the computer plotter, are not validated with data. Thus the interpretations of the deposition rates in these areas should be treated with some care.

Figure 5.5. Spatial variations of the deposition of Al ($\mu g\ m^{-2}\ day^{-1}$) at the 17 sampling locations in the lower Tamar Valley. Contour step size = 500 $\mu g\ m^{-2}\ day^{-1}$.

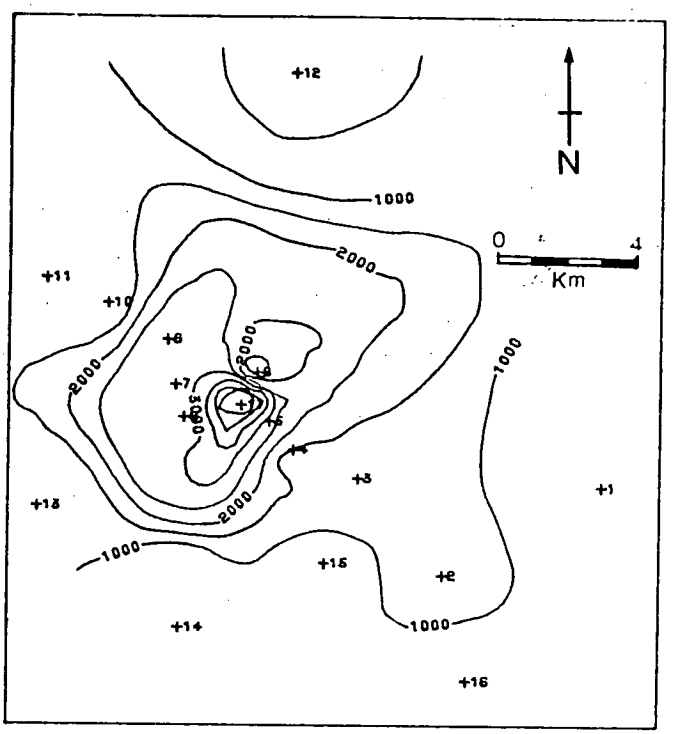


Figure 5.6. Spatial variations of the deposition of F ($\mu g\ m^{-2}\ day^{-1}$) at the 17 sampling locations in the lower Tamar Valley. Contour step size = 1000 $\mu g\ m^{-2}\ day^{-1}$ (otherwise labelled).

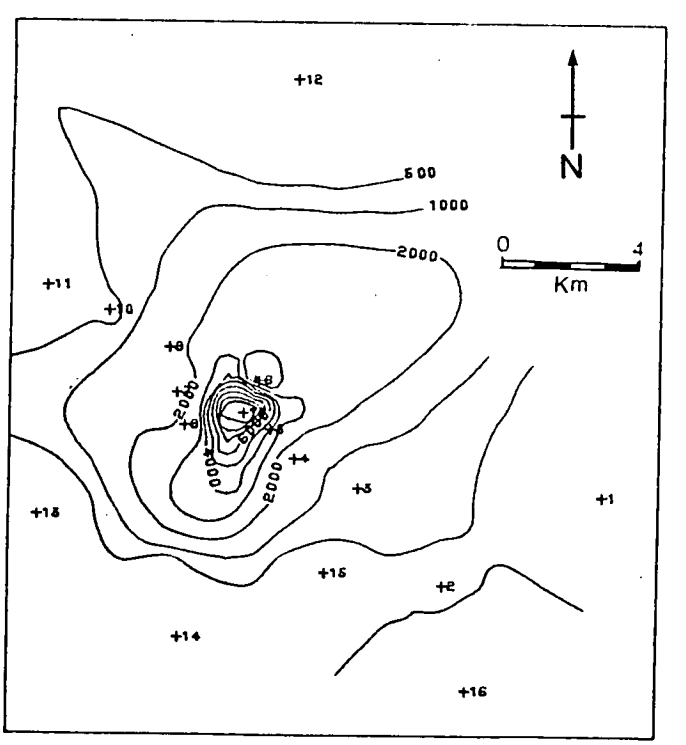


Figure 5.7. Spatial variations of the deposition of Mn(total) ($\mu g\ m^{-2}\ day^{-1}$) at the 17 sampling locations in the lower Tamar Valley. Contour step size = 500 $\mu g\ m^{-2}\ day^{-1}$ (otherwise labelled).

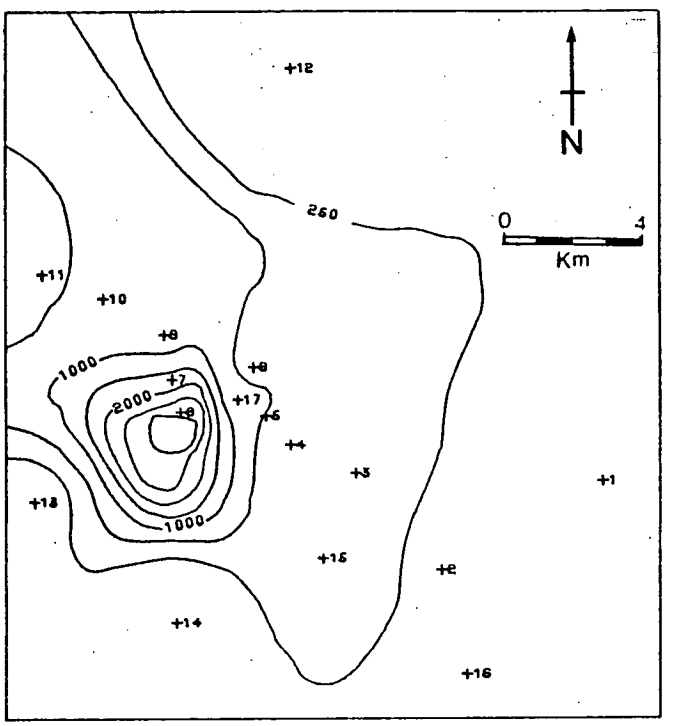
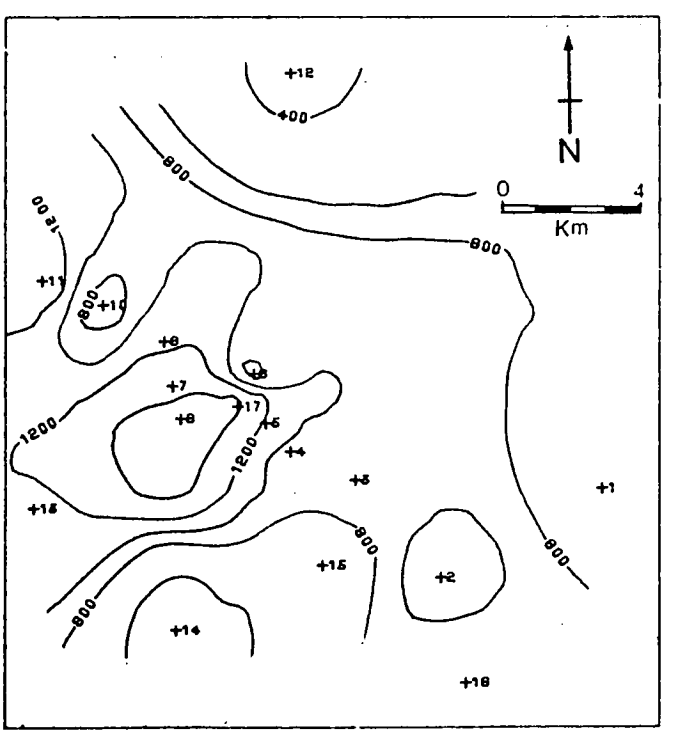


Figure 5.8. Spatial variations of the deposition of Fe ($\mu g\ m^{-2}\ day^{-1}$) at the 17 sampling locations in the lower Tamar Valley. Contour step size = 200 $\mu g\ m^{-2}$ day (otherwise labelled).



5.4.2. Deposition Rates of Zn, Cu, Ni, Cr, Co, Cd, and Pb

These heavy metals were also monitored so that they could be used for comparisons with those trace elements discussed above.

Zinc is not a good elemental tracer for air emissions from Comalco and Temco as it is not produced in these smelters. Moreover, it is abundant in the ambient air environment.

As shown in Table 5.9, the highest annual mean deposition rate of Zn was found at locations 7, with 547 $\mu g\ m^{-2}\ day^{-1}$, which was about 14 times higher than the intended 'background level (39 $\mu g\ m^{-2}\ day^{-1}$). This was followed by location 9, with 398 $\mu g\ m^{-2}\ day^{-1}$, or about 10 times higher than the intended 'background' level. While location 7 was close to the stockpiles of Temco, location 9 was close to a rubbish dump at the foothill of Mt George. The high levels of Zn at the locations were most likely to be contributed by these two sources.

Locations 11 and 13 also had significant deposition of Zn, with annual mean deposition rates about 5 and 4 times higher than the intended "background" level. Each of these sampling locations was sited near a dwelling (one in the backyard, the other in the frontyard), and also close to traffic. Zn aerosols could be produced from the abrasion of rubber tyres and automobile exhausts (Davis and and Galloway, 1981).

It seems that the deposition of Zn at each location is strongly influenced by local sources.

Soluble Zn was also significant in the deposition samples, particularly at locations 9 and 17 (Table 5.10). The distribution patterns of the soluble Zn particularly at locations more distant from the industrial sources, once again, suggest that local influence was significant.

The annual mean deposition rates of other trace metals were less significant compared with those of Al, Mn, and Fe. They varied from 1.7 to 20.8 $\mu g\ m^{-2}\ day^{-1}$ for Cu, 0.1 to 148.3 $\mu g\ m^{-2}\ day^{-1}$ for Ni, 0.1 to 3.8 $\mu g\ m^{-2}\ day^{-1}$ for Co, 0.2 to 7.2 $\mu g\ m^{-2}\ day^{-1}$ for Cr, 0.3 to 2.5 $\mu g\ m^{-2}\ day^{-1}$ for Cd, and 1.0 to 18.9 $\mu g\ m^{-2}\ day^{-1}$ for Pb (Tables 5.11 to 5.16). The deposition rates of Ni and Cu were higher at locations near the industrial areas, and the major distribution patterns appear to be similar to those of Al and F (Figures 5.9 and 5.10). The level of Pb was higher at locations close to traffic (locations 4, 6 and 13), indicating

Figure 5.9. Spatial variations of the deposition of Ni ($\mu g\ m^{-2}\ day^{-1}$) at the 17 sampling locations in the lower Tamar Valley. Contour step size = 10 $\mu g\ m^{-2}\ day^{-1}$ (otherwise labelled).

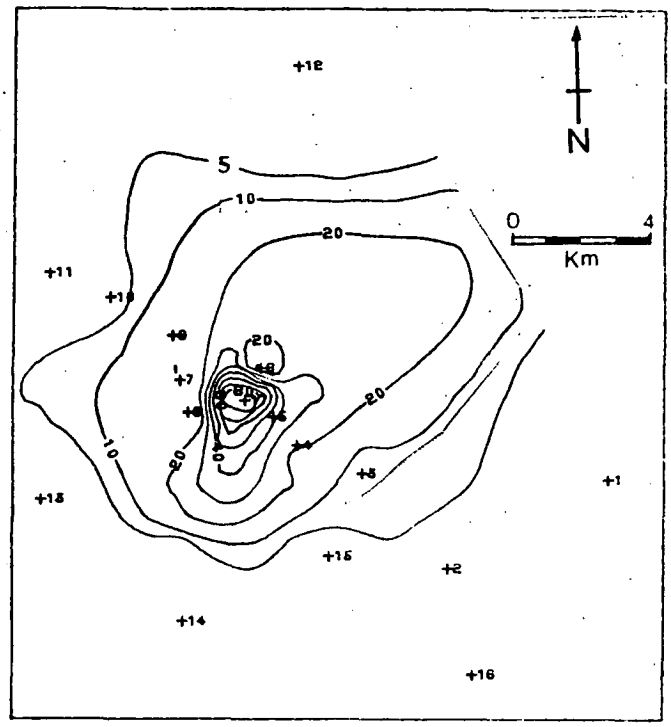


Figure 5.10. Spatial variations of the deposition of Cu ($\mu g\ m^{-2}\ day^{-1}$) at the 17 sampling locations in the lower Tamar Valley. Contour step size = 2 $\mu g\ m^{-2}\ day^{-1}$.

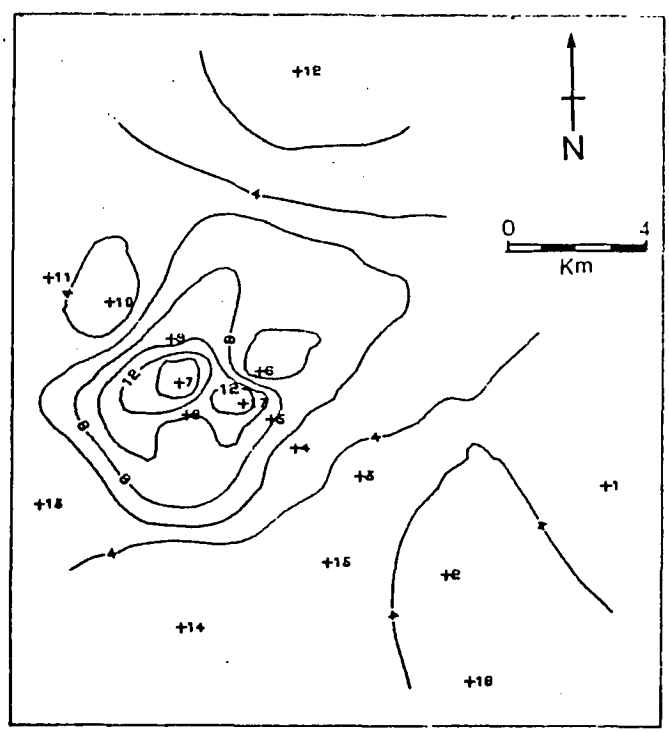
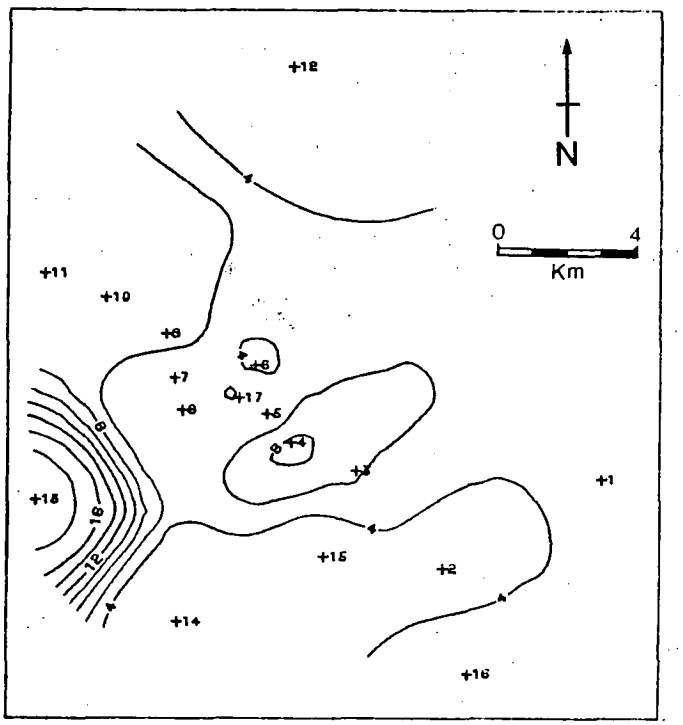


Figure 5.11. Spatial variations of the deposition of Pb ($\mu g\ m^{-2}\ day^{-1}$) at the 17 sampling locations in the lower Tamar Valley. Contour step size = 2 $\mu g\ m^{-2}\ day^{-1}$.



that it was largely contributed by the emissions of motor vehicles (Figure 5.11). The percentage compositions of these trace metals in the deposition samples were very small, with Ni and Cu both < 0.2%, Pb and Cr both < 0.02%, Co < 0.004%, and Cd < 0.003%.

5.5 Temporal Variations of Al, F, Mn and Fe Deposition

Only the four major trace elements, Al and F, Mn and Fe, which are known to be related with the air pollutants contributed by Comalco and Temco respectively, are investigated for the monthly and seasonal variations of their deposition rates. Table 5.18 gives the monthly deposition rates for these elements for all sampling locations in the lower Tamar Valley.

The highest mean deposition rates of Al and Fe for all sampling locations occurred in February 1983, while those for F and Mn (total) occurred in January and June 1983 respectively. It is difficult to generalise based on one year's data, as the variations of the monthly

mean deposition rates depend on various factors such as the meteorological parameters, chemical reactions of the elements with other constituents in the atmosphere, as well as the emission strength. Therefore the figures as given in Table 5.18 should not be regarded as 'typical'.

Table 5.18. Monthly variations of Al, F, Mn (total) and Fe deposition rates (μg m^{-2} day^{-1}), and mean wind speeds (m s^{-1}) at Station 3 in the lower Tamar Valley.

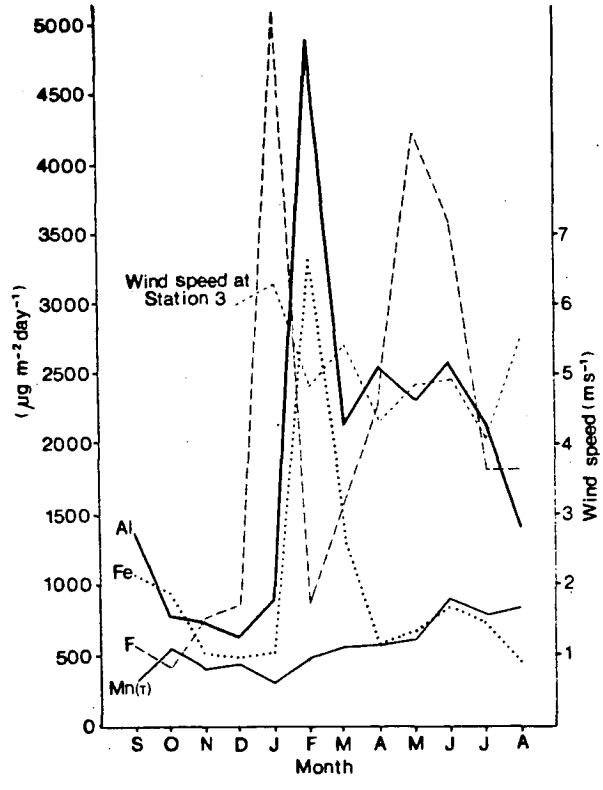
Month	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug
		(1982)							(1983)			
Element												
Al	1331	780	744	624	896	4898	2136	2662	2310	2649	2143	1406
F	562	422	755	868	5061	850	1532	2305	4211	3677	1818	1821
Mn	328	545	404	434	304	480	555	514	600	877	772	837
Fe	1072	942	503	483	515	3218	1341	577	670	840	721	444
Mean wind speed (m s^{-1}) at Station 3		-	-	6.0	6.3	4.8	5.4	4.3	4.8	4.9	4.1	5.7

The available monthly mean wind speeds at Station 3, which was 1 km ESE of Comalco, are also included in the table. In general, the lower monthly mean wind speeds, which occurred mostly in colder months, tend to correlate with higher monthly deposition rates, particularly for Al, and F (with the exception of January which had the highest deposition rate but not the lowest mean wind speed). However, the correlations between these two parameters for Mn (total) and Fe are difficult to detect (Figure 5.12). Perhaps this is to be expected as the wind field near Temco could be quite different from that near Comalco, even though they are only 1 km or so apart. This illustrates that wind data collected at a single point near a particular emission source might not be valid for another emission source nearby if the air flow is complex due to the complexity of topography between the two sources. Moriarty and Callus (1976) pointed out that situations where point observations are not representative are most often occasions of light wind and strong radiation (incoming or outgoing) in areas with marked topographical inhomogeneity such as a coast line, or mountains and valleys, as in the

case of the lower Tamar Valley.

The seasonal variations of the deposition rates of Al, F, Mn and Fe, the amount of rain collected, and the total insoluble dust for all sampling locations, as well as the mean wind speeds at Station 3 are given in Table 5.19, and illustrated in Figure 5.13.

Figure 5.12. Monthly variations of Al, F, Mn (total) and Fe deposition rates ($\mu g\ m^{-2}\ day^{-1}$), and mean wind speeds ($m\ s^{-1}$) at Station 3 in the lower Tamar Valley.



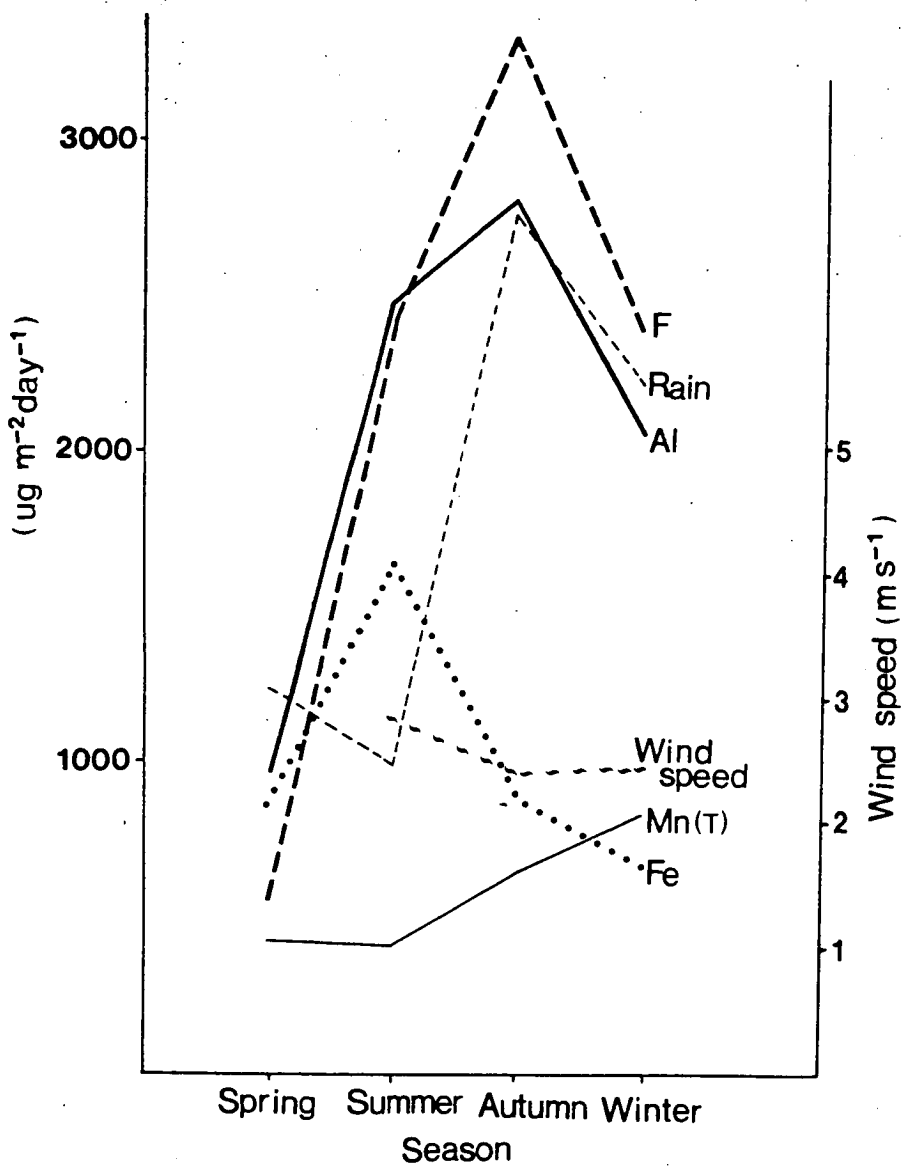
Summer was the dustiest season with a mean dust deposition level of 89 mg $m^{-2}\ day^{-1}$ for all sampling locations. The dustiness in summer was related to the lowest mean rainfall and highest mean wind speed at Station 3. However, the highest deposition rates of Al and F occurred in autumn, which also happened to have the highest amount of rain collected, and lowest mean wind speed. While Fe had the highest mean deposition rate in summer, Mn (both soluble and insoluble) had the highest mean deposition rates in winter.

Table 5.19. Seasonal Variations of Al, F, Mn(i), Mn(s), and Fe deposition rates (μg m^{-2} day^{-1}), amount of rain collected (ml m^{-2} day^{-1}), and total insoluble dust (mg m^{-2} day^{-1}) for all sampling locations, and mean wind speeds (m s^{-1}) at Station 3 in the lower Tamar Valley, September 1982 - August 1983.

Element	Season	Spring	Summer	Autumn	Winter
Al	Mean	975	2478	2807	2065
	Std. Dev.	687	2737	3926	2477
F	Mean	563	2384	3335	2393
	Std. Dev.	618	8249	5935	4196
Mn(i)	Mean	329	328	392	424
	Std. Dev.	561	503	638	821
Mn(s)	Mean	97	88	247	409
	Std. Dev.	130	147	362	1014
Fe	Mean	868	1630	895	668
	Std. Dev.	670	1674	574	757
Rain	Mean	1228	993	2757	2213
	Std. Dev.	532	1040	961	648
Dust	Mean	66	89	74	60
	Std. Dev.	60	74	88	95
Mean wind speed (m s^{-1}) at Station 3			5.7	4.8	4.9

The seasonal variations of Al and F were more or less similar, while those for Mn (total) and Fe were different (Figure 5.13). This could be due to the fact that the deposition of Fe was influenced by various local sources. The different seasonal variations between Al or F and Mn are to be expected because, as pointed out earlier, the micro-meteorological parameters which influenced the dispersion of Al or F from Comalco could be quite different from those which influenced the dispersion of Mn from Temco.

Figure 5.13. Seasonal variations of Al, F, Mn (total) and Fe deposition rates (μg m^{-2} day^{-1}), amount of rain collected (ml m^{-2} day^{-1}), total insoluble dust (mg m^{-2} day^{-1}) for all sampling locations, and mean wind speeds (m s^{-1}) at Station 3 in the lower Tamar Valley, September 1982 - August 1983.



5.6 Statistical Analysis

In order to find the inter-relationships between the levels of each trace element in the atmospheric deposition samples, the above data are analysed statistically using SPSS (Statistical Package For the Social Sciences) by Nie et al. (1975). In particular, the bivariate

correlation analysis subprogram PEARSON CORR in SPSS is used to investigate the correlations between any two trace elements and other variables such as the total insoluble dust and the amount of rain collected in the deposition samples.

Before the results of the statistical analysis are discussed, it may be appropriate first to outline the general principles of the Pearson correlation.

5.6.1 Pearson Correlation

The PEARSON CORR in SPSS computes Pearson product-moment correlations for pairs of interval-level variables. These are zero-order correlations as no controls for the influence of other variables are made. The Pearson correlation coefficient, r, is used to measure the strength of relationship between the variables, or indicate the goodness of fit of a linear regression line to the data (Nie et al., 1975).

Mathematically, r is defined as the ratio of covariation to square root of the product of the variation in X and the variation in Y, where X and Y are two variables; as given by the following formula:

$$r = \frac{\sum_{i=1}^{N}(X_i - \bar{X})(Y_i - \bar{Y})}{\left\{\left[\sum_{i=1}^{N}(X_i - \bar{X})^2\right]\left[\sum_{i=1}^{N}(Y_i - \bar{Y})^2\right]\right\}^{1/2}}$$

where X_i=ith observation of variable X

Y_i=ith observation of variable Y

N= number of observations

$\bar{X} = \sum_{i=1}^{N} X_i/N$ = mean of variable X

$\bar{Y} = \sum_{i=1}^{N} Y_i/N$ = mean of variable Y

The actual formula used by SPSS for computing Pearson Correlation Coefficients, r, is:

$$r = \frac{\sum_{i=1}^{N} X_i Y_i - \left(\sum_{i=1}^{N} X_i\right)\left(\sum_{i=1}^{N} Y_i\right)/N}{\left\{\left[\sum_{i=1}^{N} X_i^2 - \left(\sum_{i=1}^{N} X_i\right)^2/N\right]\left[\sum_{i=1}^{N} Y_i^2 - \left(\sum_{i=1}^{N} Y_i\right)^2/N\right]\right\}^{1/2}}$$

It must be noted that Pearson r reflects only the linear relationship between two variables. It varies between values of -1.00 (perfect negative relationship) to +1.00 (perfect positive relationship), and a coefficient of zero represents the absence of a relationship between the two variables (Nie et al., 1975; McCall, 1982).

Significance tests are reported for each coefficient. These are derived from the use of Student's t with N-2 degrees of freedom for the computed quantity:

$$r\left[\frac{N-2}{1-r^2}\right]^{1/2}$$

The output of the PEARSON CORR subprogram in SPSS includes the coefficient , r, the number of cases, N, upon which r was computed, and the test of significance, p. These are given in a matrix of correlation as requested.

Cases containing missing values are excluded from the computation pairwise, i.e. a case is deleted from the computation of a given coefficient when either of the variables involved in that coefficient is missing; that case will, however, be included in the computation of all coefficients for which there is complete information for that case (Nie et al., 1975).

Further details on PEARSON CORR can be found in Nie et al. (1975).

5.6.2 Correlations of Al, F, Mn and Fe with Other Elements or Variables

The annual (from September 1982 to August 1983) and seasonal correlations between the deposition rates of each trace element for all locations are investigated statistically. The Pearson correlation coefficients between any two elements or variables for the year, spring, summer, autumn, and winter are calculated and given in Tables 5.20 to 5.24 respectively. The following discussion is mainly focused on the correlations of Al, F, Mn, and Fe with other trace elements and variables.

Table 5.20. Pearson correlation matrix for various variables for the year, September 1982 - August 1983.

----------PEARSON CORRELATION COEFFICIENTS----------

	AL	MNI	FE	ZNI	NI	MNS	ZNS	CU	PB	CO	CR	CD	DUST	RAIN	F
AL	1.0000	0.3508	0.5572	0.2215	0.7041	0.1230	0.0473	0.6512	0.1123	0.6805	0.2217	0.1328	0.4379	0.0360	0.4791
	(234)	(233)	(234)	(234)	(234)	(225)	(225)	(233)	(189)	(189)	(234)	(189)	(233)	(230)	(216)
	P=*****	P=0.000	P=0.000	P=0.000	P=0.000	P=0.033	P=0.240	P=0.000	P=0.062	P=0.000	P=0.000	P=0.034	P=0.000	P=0.294	P=0.000
MNI	0.3508	1.0000	0.1804	0.1618	0.0731	0.3068	0.0108	0.2439	-0.0253	0.2737	-0.0114	0.0218	0.2498	-0.0360	0.0238
	(233)	(233)	(233)	(233)	(233)	(224)	(224)	(232)	(189)	(189)	(233)	(189)	(232)	(229)	(215)
	P=0.000	P=*****	P=0.003	P=0.007	P=0.133	P=0.000	P=0.436	P=0.000	P=0.365	P=0.000	P=0.431	P=0.383	P=0.000	P=0.294	P=0.364
FE	0.5572	0.1804	1.0000	0.3212	0.2491	0.0541	0.0301	0.4202	0.3903	0.3588	0.5445	0.2894	0.4407	-0.2424	0.1274
	(234)	(233)	(234)	(234)	(234)	(225)	(225)	(233)	(189)	(189)	(234)	(189)	(233)	(230)	(216)
	P=0.000	P=0.003	P=*****	P=0.000	P=0.000	P=0.210	P=0.327	P=0.000	P=0.000	P=0.000	P=0.000	P=0.000	P=0.000	P=0.000	P=0.031
ZNI	0.2215	0.1618	0.3212	1.0000	0.1228	-0.0305	0.2095	0.3012	0.3249	0.3068	0.1980	0.3472	0.5237	-0.0773	0.0569
	(234)	(233)	(234)	(234)	(234)	(225)	(225)	(233)	(189)	(189)	(234)	(189)	(233)	(230)	(216)
	P=0.000	P=0.007	P=0.000	P=*****	P=0.030	P=0.325	P=0.001	P=0.000	P=0.000	P=0.000	P=0.001	P=0.000	P=0.000	P=0.121	P=0.203
NI	0.7041	0.0731	0.2491	0.1228	1.0000	0.0319	0.1325	0.6374	0.0582	0.8288	0.0919	0.0126	0.2192	0.1653	0.6992
	(234)	(233)	(234)	(234)	(234)	(225)	(225)	(233)	(189)	(189)	(234)	(189)	(233)	(230)	(216)
	P=0.000	P=0.133	P=0.000	P=0.030	P=*****	P=0.317	P=0.024	P=0.000	P=0.213	P=0.000	P=0.081	P=0.432	P=0.000	P=0.006	P=0.000
MNS	0.1230	0.3068	0.0541	-0.0305	0.0319	1.0000	0.0705	0.1662	-0.0889	0.1368	-0.0033	-0.0397	0.1293	0.1861	0.0991
	(225)	(224)	(225)	(225)	(225)	(227)	(227)	(225)	(183)	(183)	(226)	(183)	(226)	(227)	(213)
	P=0.033	P=0.000	P=0.210	P=0.325	P=0.317	P=*****	P=0.145	P=0.006	P=0.116	P=0.032	P=0.481	P=0.297	P=0.026	P=0.002	P=0.075
ZNS	0.0473	0.0108	0.0301	0.2095	0.1325	0.0705	1.0000	0.1715	0.0045	0.2142	0.0462	0.2815	0.0769	0.2652	0.1992
	(225)	(224)	(225)	(225)	(225)	(227)	(227)	(225)	(183)	(183)	(226)	(183)	(226)	(227)	(213)
	P=0.240	P=0.436	P=0.327	P=0.001	P=0.024	P=0.145	P=*****	P=0.005	P=0.476	P=0.002	P=0.245	P=0.000	P=0.125	P=0.000	P=0.002
CU	0.6512	0.2439	0.4202	0.3012	0.6374	0.1662	0.1715	1.0000	0.1872	0.6648	0.3671	0.2577	0.6374	0.2180	0.4749
	(233)	(232)	(233)	(233)	(233)	(225)	(225)	(234)	(189)	(189)	(234)	(189)	(233)	(230)	(216)
	P=0.000	P=0.000	P=0.000	P=0.000	P=0.000	P=0.006	P=0.005	P=*****	P=0.005	P=0.000	P=0.000	P=0.000	P=0.000	P=0.000	P=0.000
PB	0.1123	-0.0253	0.3903	0.3249	0.0582	-0.0889	0.0045	0.1872	1.0000	0.2156	0.3562	0.2790	0.1719	-0.0582	-0.0252
	(189)	(189)	(189)	(189)	(189)	(183)	(183)	(189)	(190)	(190)	(190)	(190)	(189)	(187)	(178)
	P=0.062	P=0.365	P=0.000	P=0.000	P=0.213	P=0.116	P=0.476	P=0.005	P=*****	P=0.001	P=0.000	P=0.000	P=0.009	P=0.214	P=0.369
CO	0.6805	0.2737	0.3588	0.3068	0.8288	0.1368	0.2142	0.6648	0.2156	1.0000	0.0932	0.0919	0.3553	0.1268	0.5715
	(189)	(189)	(189)	(189)	(189)	(183)	(183)	(189)	(190)	(190)	(190)	(190)	(189)	(187)	(178)
	P=0.000	P=0.000	P=0.000	P=0.000	P=0.000	P=0.032	P=0.002	P=0.000	P=0.001	P=*****	P=0.100	P=0.104	P=0.000	P=0.042	P=0.000
CR	0.2217	-0.0114	0.5445	0.1980	0.0919	-0.0033	0.0462	0.3671	0.3562	0.0932	1.0000	0.5687	0.2809	-0.1635	0.0860
	(234)	(233)	(234)	(234)	(234)	(226)	(226)	(234)	(190)	(190)	(235)	(190)	(234)	(231)	(217)
	P=0.000	P=0.431	P=0.000	P=0.001	P=0.081	P=0.481	P=0.245	P=0.000	P=0.000	P=0.100	P=*****	P=0.000	P=0.000	P=0.006	P=0.103
CD	0.1328	0.0218	0.2894	0.3472	0.0126	-0.0397	0.2815	0.2577	0.2790	0.0919	0.5687	1.0000	0.1621	-0.0748	0.0014
	(189)	(189)	(189)	(189)	(189)	(183)	(183)	(189)	(190)	(190)	(190)	(190)	(189)	(187)	(178)
	P=0.034	P=0.383	P=0.000	P=0.000	P=0.432	P=0.297	P=0.000	P=0.000	P=0.000	P=0.104	P=0.000	P=*****	P=0.013	P=0.154	P=0.492
DUST	0.4379	0.2498	0.4407	0.5237	0.2192	0.1293	0.0769	0.6374	0.1719	0.3553	0.2809	0.1621	1.0000	0.0019	0.1449
	(233)	(232)	(233)	(233)	(233)	(226)	(226)	(233)	(189)	(189)	(234)	(189)	(235)	(231)	(217)
	P=0.000	P=0.000	P=0.000	P=0.000	P=0.000	P=0.026	P=0.125	P=0.000	P=0.009	P=0.000	P=0.000	P=0.013	P=*****	P=0.489	P=0.016
RAIN	0.0360	-0.0360	-0.2424	-0.0773	0.1653	0.1861	0.2652	0.2180	-0.0582	0.1268	-0.1635	-0.0748	0.0019	1.0000	0.2242
	(230)	(229)	(230)	(230)	(230)	(227)	(227)	(230)	(187)	(187)	(231)	(187)	(231)	(232)	(216)
	P=0.294	P=0.294	P=0.000	P=0.121	P=0.006	P=0.002	P=0.000	P=0.000	P=0.214	P=0.042	P=0.006	P=0.154	P=0.489	P=*****	P=0.000
F	0.4791	0.0238	0.1274	0.0569	0.6992	0.0991	0.1992	0.4749	-0.0252	0.5715	0.0860	0.0014	0.1449	0.2242	1.0000
	(216)	(215)	(216)	(216)	(216)	(213)	(213)	(216)	(178)	(178)	(217)	(178)	(217)	(216)	(218)
	P=0.000	P=0.364	P=0.031	P=0.203	P=0.000	P=0.075	P=0.002	P=0.000	P=0.369	P=0.000	P=0.103	P=0.492	P=0.016	P=0.000	P=*****

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Table 5.21. Pearson correlation matrix for various variables for Spring 1982.

----------PEARSON CORRELATION COEFFICIENTS----------

	AL	MNI	FE	ZNI	NI	MNS	ZNS	CU	PB	CO	CR	CD	DUST	RAIN	F
AL	1.0000	0.4501	0.7247	0.5495	0.6291	0.0543	0.1033	0.7348	0.1640	0.2261	0.6261	0.1176	0.7111	0.4035	0.4234
	(43)	(42)	(43)	(43)	(43)	(42)	(42)	(43)	(31)	(31)	(43)	(31)	(43)	(43)	(42)
	P=*****	P=0.001	P=0.000	P=0.000	P=0.000	P=0.366	P=0.258	P=0.000	P=0.189	P=0.111	P=0.000	P=0.264	P=0.000	P=0.004	P=0.003
MNI	0.4501	1.0000	0.3549	0.2485	0.3087	0.2186	-0.0801	0.4187	0.0306	0.2307	0.1974	0.0414	0.6300	-0.0911	0.0862
	(42)	(42)	(42)	(42)	(42)	(41)	(41)	(42)	(31)	(31)	(42)	(31)	(42)	(42)	(41)
	P=0.001	P=*****	P=0.011	P=0.056	P=0.023	P=0.085	P=0.309	P=0.003	P=0.435	P=0.106	P=0.105	P=0.413	P=0.000	P=0.283	P=0.296
FE	0.7247	0.3549	1.0000	0.4859	0.4487	0.0473	0.2864	0.8555	0.4146	0.4742	0.8089	0.1563	0.6772	0.3151	0.2386
	(43)	(42)	(43)	(43)	(43)	(42)	(42)	(43)	(31)	(31)	(43)	(31)	(43)	(43)	(42)
	P=0.000	P=0.011	P=*****	P=0.000	P=0.001	P=0.383	P=0.033	P=0.000	P=0.010	P=0.004	P=0.000	P=0.201	P=0.000	P=0.020	P=0.064
ZNI	0.5495	0.2485	0.4859	1.0000	0.0481	-0.0778	0.2443	0.4861	0.5779	0.6618	0.6598	0.4152	0.4891	0.2113	-0.0651
	(43)	(42)	(43)	(43)	(43)	(42)	(42)	(43)	(31)	(31)	(43)	(31)	(43)	(43)	(42)
	P=0.000	P=0.056	P=0.000	P=*****	P=0.380	P=0.312	P=0.059	P=0.000	P=0.000	P=0.000	P=0.000	P=0.010	P=0.000	P=0.087	P=0.341
NI	0.6291	0.3087	0.4487	0.0481	1.0000	0.2258	-0.1643	0.5606	-0.1148	0.0792	0.2437	-0.1540	0.4128	0.1303	0.8844
	(43)	(42)	(43)	(43)	(43)	(42)	(42)	(43)	(31)	(31)	(43)	(31)	(43)	(43)	(42)
	P=0.000	P=0.023	P=0.001	P=0.380	P=*****	P=0.075	P=0.149	P=0.000	P=0.269	P=0.336	P=0.058	P=0.204	P=0.003	P=0.202	P=0.000
MNS	0.0543	0.2186	0.0473	-0.0778	0.2258	1.0000	-0.0707	0.1795	-0.1926	-0.0404	-0.1560	-0.1175	0.2577	0.1180	0.1011
	(42)	(41)	(42)	(42)	(42)	(42)	(42)	(42)	(31)	(31)	(42)	(31)	(42)	(42)	(42)
	P=0.366	P=0.085	P=0.383	P=0.312	P=0.075	P=*****	P=0.328	P=0.128	P=0.150	P=0.415	P=0.162	P=0.265	P=0.050	P=0.228	P=0.262
ZNS	0.1033	-0.0801	0.2864	0.2443	-0.1643	-0.0707	1.0000	0.2072	0.3123	0.1472	0.2280	0.3866	-0.0064	0.1510	-0.1136
	(42)	(41)	(42)	(42)	(42)	(42)	(42)	(42)	(31)	(31)	(42)	(31)	(42)	(42)	(42)
	P=0.258	P=0.309	P=0.033	P=0.059	P=0.149	P=0.328	P=*****	P=0.094	P=0.044	P=0.215	P=0.073	P=0.016	P=0.484	P=0.170	P=0.237
CU	0.7348	0.4187	0.8555	0.4861	0.5606	0.1795	0.2072	1.0000	0.3383	0.5178	0.6476	0.0733	0.7454	0.3290	0.3268
	(43)	(42)	(43)	(43)	(43)	(42)	(42)	(43)	(31)	(31)	(43)	(31)	(43)	(43)	(42)
	P=0.000	P=0.003	P=0.000	P=0.000	P=0.000	P=0.128	P=0.094	P=*****	P=0.031	P=0.001	P=0.000	P=0.348	P=0.000	P=0.016	P=0.017
PB	0.1640	0.0306	0.4146	0.5779	-0.1148	-0.1926	0.3123	0.3383	1.0000	0.7690	0.5843	0.2731	0.2149	-0.0804	-0.1685
	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)
	P=0.189	P=0.435	P=0.010	P=0.000	P=0.269	P=0.150	P=0.044	P=0.031	P=*****	P=0.000	P=0.000	P=0.069	P=0.123	P=0.334	P=0.182
CO	0.2261	0.2307	0.4742	0.6618	0.0792	-0.0404	0.1472	0.5178	0.7690	1.0000	0.4964	0.3120	0.3592	-0.1300	-0.0079
	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)
	P=0.111	P=0.106	P=0.004	P=0.000	P=0.336	P=0.415	P=0.215	P=0.001	P=0.000	P=*****	P=0.002	P=0.044	P=0.024	P=0.243	P=0.483
CR	0.6261	0.1974	0.8089	0.6598	0.2437	-0.1560	0.2280	0.6476	0.5843	0.4964	1.0000	0.1603	0.5563	0.1753	0.0971
	(43)	(42)	(43)	(43)	(43)	(42)	(42)	(43)	(31)	(31)	(43)	(31)	(43)	(43)	(42)
	P=0.000	P=0.105	P=0.000	P=0.000	P=0.058	P=0.162	P=0.073	P=0.000	P=0.000	P=0.002	P=*****	P=0.194	P=0.000	P=0.130	P=0.270
CD	0.1176	0.0414	0.1563	0.4152	-0.1540	-0.1175	0.3866	0.0733	0.2731	0.3120	0.1603	1.0000	0.0429	0.3376	-0.1305
	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)	(31)
	P=0.264	P=0.413	P=0.201	P=0.010	P=0.204	P=0.265	P=0.016	P=0.348	P=0.069	P=0.044	P=0.194	P=*****	P=0.409	P=0.032	P=0.242
DUST	0.7111	0.6300	0.6772	0.4891	0.4128	0.2577	-0.0064	0.7454	0.2149	0.3592	0.5563	0.0429	1.0000	0.1840	0.1813
	(43)	(42)	(43)	(43)	(43)	(42)	(42)	(43)	(31)	(31)	(43)	(31)	(43)	(43)	(42)
	P=0.000	P=0.000	P=0.000	P=0.000	P=0.003	P=0.050	P=0.484	P=0.000	P=0.123	P=0.024	P=0.000	P=0.409	P=*****	P=0.119	P=0.125
RAIN	0.4035	-0.0911	0.3151	0.2113	0.1303	0.1180	0.1510	0.3290	-0.0804	-0.1300	0.1753	0.3376	0.1840	1.0000	-0.0576
	(43)	(42)	(43)	(43)	(43)	(42)	(42)	(43)	(31)	(31)	(43)	(31)	(43)	(43)	(42)
	P=0.004	P=0.283	P=0.020	P=0.087	P=0.202	P=0.228	P=0.170	P=0.016	P=0.334	P=0.243	P=0.130	P=0.032	P=0.119	P=*****	P=0.359
F	0.4234	0.0862	0.2386	-0.0651	0.8844	0.1011	-0.1136	0.3268	-0.1685	-0.0079	0.0971	-0.1305	0.1813	-0.0576	1.0000
	(42)	(41)	(42)	(42)	(42)	(42)	(42)	(42)	(31)	(31)	(42)	(31)	(42)	(42)	(42)
	P=0.003	P=0.296	P=0.064	P=0.341	P=0.000	P=0.262	P=0.237	P=0.017	P=0.182	P=0.483	P=0.270	P=0.242	P=0.125	P=0.359	P=*****

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Table 5.22. Pearson correlation matrix for various variables for Summer 1982-83.

----------PEARSON CORRELATION COEFFICIENTS----------

	AL	MNI	FE	ZNI	NI	MNS	ZNS	CU	PB	CO	CR	CD	DUST	RAIN	F
AL	1.0000	0.4354	0.7637	0.1026	0.4313	-0.1278	-0.1340	0.3865	0.1395	0.2478	0.2235	-0.0431	0.3459	-0.5707	0.0650
	(56)	(56)	(56)	(56)	(56)	(54)	(54)	(55)	(23)	(23)	(56)	(23)	(56)	(54)	(49)
	P=*****	P=0.000	P=0.000	P=0.226	P=0.000	P=0.179	P=0.167	P=0.002	P=0.263	P=0.127	P=0.049	P=0.423	P=0.005	P=0.000	P=0.329
MNI	0.4354	1.0000	0.2870	0.1844	0.0536	0.0587	0.0114	0.1011	-0.0837	0.0842	-0.0780	-0.1812	0.3322	-0.0724	-0.0425
	(56)	(56)	(56)	(56)	(56)	(54)	(54)	(55)	(23)	(23)	(56)	(23)	(56)	(54)	(49)
	P=0.000	P=*****	P=0.016	P=0.087	P=0.348	P=0.337	P=0.467	P=0.231	P=0.352	P=0.351	P=0.284	P=0.204	P=0.006	P=0.302	P=0.386
FE	0.7637	0.2870	1.0000	0.2083	0.1087	-0.1933	-0.1348	0.5458	0.7932	-0.2896	0.5243	0.5194	0.4504	-0.5979	-0.0882
	(56)	(56)	(56)	(56)	(56)	(54)	(54)	(55)	(23)	(23)	(56)	(23)	(56)	(54)	(49)
	P=0.000	P=0.016	P=*****	P=0.062	P=0.212	P=0.081	P=0.166	P=0.000	P=0.000	P=0.090	P=0.000	P=0.006	P=0.000	P=0.000	P=0.273
ZNI	0.1026	0.1844	0.2083	1.0000	-0.0448	-0.0787	0.1496	0.1601	-0.0233	-0.0062	0.1073	0.3195	0.5922	-0.1174	-0.0669
	(56)	(56)	(56)	(56)	(56)	(54)	(54)	(55)	(23)	(23)	(56)	(23)	(56)	(54)	(49)
	P=0.226	P=0.087	P=0.062	P=*****	P=0.371	P=0.286	P=0.140	P=0.121	P=0.458	P=0.489	P=0.216	P=0.069	P=0.000	P=0.199	P=0.324
NI	0.4313	0.0536	0.1087	-0.0448	1.0000	-0.0846	0.0755	0.2416	-0.4085	0.8977	-0.0518	-0.2220	0.0281	-0.2394	0.3691
	(56)	(56)	(56)	(56)	(56)	(54)	(54)	(55)	(23)	(23)	(56)	(23)	(56)	(54)	(49)
	P=0.000	P=0.348	P=0.212	P=0.371	P=*****	P=0.272	P=0.294	P=0.038	P=0.026	P=0.000	P=0.352	P=0.154	P=0.419	P=0.041	P=0.005
MNS	-0.1278	0.0587	-0.1933	-0.0787	-0.0846	1.0000	0.3283	0.0469	0.4922	-0.1018	0.0889	0.8031	-0.1926	0.2701	0.1534
	(54)	(54)	(54)	(54)	(54)	(55)	(55)	(53)	(22)	(22)	(54)	(22)	(55)	(55)	(48)
	P=0.179	P=0.337	P=0.081	P=0.286	P=0.272	P=*****	P=0.007	P=0.369	P=0.010	P=0.326	P=0.261	P=0.000	P=0.079	P=0.023	P=0.149
ZNS	-0.1340	0.0114	-0.1348	0.1496	0.0755	0.3283	1.0000	0.1019	-0.0063	0.3247	0.0352	0.2270	-0.0651	0.3347	0.1586
	(54)	(54)	(54)	(54)	(54)	(55)	(55)	(53)	(22)	(22)	(54)	(22)	(55)	(55)	(48)
	P=0.167	P=0.467	P=0.166	P=0.140	P=0.294	P=0.007	P=*****	P=0.234	P=0.489	P=0.070	P=0.400	P=0.155	P=0.318	P=0.006	P=0.141
CU	0.3865	0.1011	0.5458	0.1601	0.2416	0.0469	0.1019	1.0000	0.6349	-0.0170	0.8272	0.7984	0.4454	-0.1642	0.1267
	(55)	(55)	(55)	(55)	(55)	(53)	(53)	(55)	(22)	(22)	(55)	(22)	(55)	(53)	(48)
	P=0.002	P=0.231	P=0.000	P=0.121	P=0.038	P=0.369	P=0.234	P=*****	P=0.001	P=0.470	P=0.000	P=0.000	P=0.000	P=0.120	P=0.195
PB	0.1395	-0.0837	0.7932	-0.0233	-0.4085	0.4922	-0.0063	0.6349	1.0000	-0.4694	0.7233	0.6257	0.4717	0.1030	-0.2448
	(23)	(23)	(23)	(23)	(23)	(22)	(22)	(22)	(23)	(23)	(23)	(23)	(23)	(22)	(21)
	P=0.263	P=0.352	P=0.000	P=0.458	P=0.026	P=0.010	P=0.489	P=0.001	P=*****	P=0.012	P=0.000	P=0.001	P=0.012	P=0.324	P=0.142
CO	0.2478	0.0842	-0.2896	-0.0062	0.8977	-0.1018	0.3247	-0.0170	-0.4694	1.0000	-0.3101	-0.2894	-0.0271	0.0964	0.2237
	(23)	(23)	(23)	(23)	(23)	(22)	(22)	(22)	(23)	(23)	(23)	(23)	(23)	(22)	(21)
	P=0.127	P=0.351	P=0.090	P=0.489	P=0.000	P=0.326	P=0.070	P=0.470	P=0.012	P=*****	P=0.075	P=0.090	P=0.451	P=0.335	P=0.165
CR	0.2235	-0.0780	0.5243	0.1073	-0.0518	0.0889	0.0352	0.8272	0.7233	-0.3101	1.0000	0.9017	0.3190	-0.2221	-0.0192
	(56)	(56)	(56)	(56)	(56)	(54)	(54)	(55)	(23)	(23)	(56)	(23)	(56)	(54)	(49)
	P=0.049	P=0.284	P=0.000	P=0.216	P=0.352	P=0.261	P=0.400	P=0.000	P=0.000	P=0.075	P=*****	P=0.000	P=0.008	P=0.053	P=0.448
CD	-0.0431	-0.1812	0.5194	0.3195	-0.2220	0.8031	0.2270	0.7984	0.6257	-0.2894	0.9017	1.0000	0.4359	-0.2569	-0.1279
	(23)	(23)	(23)	(23)	(23)	(22)	(22)	(22)	(23)	(23)	(23)	(23)	(23)	(22)	(21)
	P=0.423	P=0.204	P=0.006	P=0.069	P=0.154	P=0.000	P=0.155	P=0.000	P=0.001	P=0.090	P=0.000	P=*****	P=0.019	P=0.124	P=0.290
DUST	0.3459	0.3322	0.4504	0.5922	0.0281	-0.1926	-0.0651	0.4454	0.4717	-0.0271	0.3190	0.4359	1.0000	-0.1962	-0.0402
	(56)	(56)	(56)	(56)	(56)	(55)	(55)	(55)	(23)	(23)	(56)	(23)	(57)	(55)	(50)
	P=0.005	P=0.006	P=0.000	P=0.000	P=0.419	P=0.079	P=0.318	P=0.000	P=0.012	P=0.451	P=0.008	P=0.019	P=*****	P=0.076	P=0.391
RAIN	-0.5707	-0.0724	-0.5979	-0.1174	-0.2394	0.2701	0.3347	-0.1642	0.1030	0.0964	-0.2221	-0.2569	-0.1962	1.0000	-0.0748
	(54)	(54)	(54)	(54)	(54)	(55)	(55)	(53)	(22)	(22)	(54)	(22)	(55)	(55)	(48)
	P=0.000	P=0.302	P=0.000	P=0.199	P=0.041	P=0.023	P=0.006	P=0.120	P=0.324	P=0.335	P=0.053	P=0.124	P=0.076	P=*****	P=0.307
F	0.0650	-0.0425	-0.0882	-0.0669	0.3691	0.1534	0.1586	0.1267	-0.2448	0.2237	-0.0192	-0.1279	-0.0402	-0.0748	1.0000
	(49)	(49)	(49)	(49)	(49)	(48)	(48)	(48)	(21)	(21)	(49)	(21)	(50)	(48)	(50)
	P=0.329	P=0.386	P=0.273	P=0.324	P=0.005	P=0.149	P=0.141	P=0.195	P=0.142	P=0.165	P=0.448	P=0.290	P=0.391	P=0.307	P=*****

(COEFFICIENT / (CASES) / SIGNIFICANCE) (A VALUE OF 99.0000 IS PRINTED IF A COEFFICIENT CANNOT BE COMPUTED)

Table 5.23. Pearson correlation matrix for various variables for Autumn 1983.

----------PEARSON CORRELATION COEFFICIENTS----------

	AL	MNI	FE	ZNI	NI	MNS	ZNS	CU	PB	CO	CR	CD	DUST	RAIN	F
AL	1.0000	0.6081	0.5522	0.3532	0.7281	0.1300	0.0622	0.6506	0.1881	0.7366	0.3853	0.2029	0.4625	0.0677	0.6575
	(64)	(64)	(64)	(64)	(64)	(62)	(62)	(64)	(64)	(64)	(64)	(64)	(63)	(63)	(57)
	P=*****	P=0.000	P=0.000	P=0.002	P=0.000	P=0.157	P=0.316	P=0.000	P=0.068	P=0.000	P=0.001	P=0.054	P=0.000	P=0.299	P=0.000
MNI	0.6081	1.0000	0.4238	0.3108	0.1053	0.3448	0.0961	0.3894	-0.0179	0.2612	0.0055	0.2741	0.3713	-0.0204	0.0598
	(64)	(64)	(64)	(64)	(64)	(62)	(62)	(64)	(64)	(64)	(64)	(64)	(63)	(63)	(57)
	P=0.000	P=*****	P=0.000	P=0.006	P=0.204	P=0.003	P=0.229	P=0.001	P=0.444	P=0.019	P=0.483	P=0.014	P=0.001	P=0.437	P=0.329
FE	0.5522	0.4238	1.0000	0.3775	0.5413	0.3515	0.2379	0.5512	0.4098	0.7043	0.5534	0.0920	0.4271	0.4202	0.4607
	(64)	(64)	(64)	(64)	(64)	(62)	(62)	(64)	(64)	(64)	(64)	(64)	(63)	(63)	(57)
	P=0.000	P=0.000	P=*****	P=0.001	P=0.000	P=0.003	P=0.031	P=0.000	P=0.000	P=0.000	P=0.000	P=0.235	P=0.000	P=0.000	P=0.000
ZNI	0.3532	0.3108	0.3775	1.0000	0.3248	0.0633	0.3693	0.5464	0.0498	0.3832	0.1273	0.2601	0.6429	0.1156	0.2435
	(64)	(64)	(64)	(64)	(64)	(62)	(62)	(64)	(64)	(64)	(64)	(64)	(63)	(63)	(57)
	P=0.002	P=0.006	P=0.001	P=*****	P=0.004	P=0.313	P=0.002	P=0.000	P=0.348	P=0.001	P=0.158	P=0.019	P=0.000	P=0.184	P=0.034
NI	0.7281	0.1053	0.5413	0.3248	1.0000	0.1976	0.1277	0.6590	0.3311	0.9242	0.5087	0.0895	0.3104	0.0070	0.8923
	(64)	(64)	(64)	(64)	(64)	(62)	(62)	(64)	(64)	(64)	(64)	(64)	(63)	(63)	(57)
	P=0.000	P=0.204	P=0.000	P=0.004	P=*****	P=0.062	P=0.161	P=0.000	P=0.004	P=0.000	P=0.000	P=0.241	P=0.007	P=0.478	P=0.000
MNS	0.1300	0.3448	0.3515	0.0633	0.1976	1.0000	0.1763	0.1039	-0.0297	0.0736	0.0962	0.0160	0.2063	0.1331	0.2643
	(62)	(62)	(62)	(62)	(62)	(63)	(63)	(63)	(63)	(63)	(63)	(63)	(62)	(63)	(58)
	P=0.157	P=0.003	P=0.003	P=0.313	P=0.062	P=*****	P=0.083	P=0.209	P=0.409	P=0.283	P=0.227	P=0.450	P=0.054	P=0.149	P=0.022
ZNS	0.0622	0.0961	0.2379	0.3693	0.1277	0.1763	1.0000	0.1222	0.0140	0.2368	-0.0078	0.4806	0.0817	0.1804	0.2099
	(62)	(62)	(62)	(62)	(62)	(63)	(63)	(63)	(63)	(63)	(63)	(63)	(62)	(63)	(58)
	P=0.316	P=0.229	P=0.031	P=0.002	P=0.161	P=0.083	P=*****	P=0.170	P=0.457	P=0.031	P=0.476	P=0.000	P=0.264	P=0.079	P=0.057
CU	0.6506	0.3894	0.5512	0.5464	0.6590	0.1039	0.1222	1.0000	0.2503	0.6958	0.4732	0.2337	0.7530	-0.0443	0.6018
	(64)	(64)	(64)	(64)	(64)	(63)	(63)	(65)	(65)	(65)	(65)	(65)	(64)	(64)	(58)
	P=0.000	P=0.001	P=0.000	P=0.000	P=0.000	P=0.209	P=0.170	P=*****	P=0.022	P=0.000	P=0.000	P=0.030	P=0.000	P=0.364	P=0.000
PB	0.1881	-0.0179	0.4098	0.0498	0.3311	-0.0297	0.0140	0.2503	1.0000	0.3729	0.2724	0.0507	0.1419	0.3694	0.2218
	(64)	(64)	(64)	(64)	(64)	(63)	(63)	(65)	(65)	(65)	(65)	(65)	(64)	(64)	(58)
	P=0.068	P=0.444	P=0.000	P=0.348	P=0.004	P=0.409	P=0.457	P=0.022	P=*****	P=0.001	P=0.014	P=0.344	P=0.132	P=0.001	P=0.047
CO	0.7366	0.2612	0.7043	0.3832	0.9242	0.0736	0.2368	0.6958	0.3729	1.0000	0.5083	0.1825	0.3298	0.0966	0.8212
	(64)	(64)	(64)	(64)	(64)	(63)	(63)	(65)	(65)	(65)	(65)	(65)	(64)	(64)	(58)
	P=0.000	P=0.019	P=0.000	P=0.001	P=0.000	P=0.283	P=0.031	P=0.000	P=0.001	P=*****	P=0.000	P=0.073	P=0.004	P=0.224	P=0.000
CR	0.3853	0.0055	0.5534	0.1273	0.5087	0.0962	-0.0078	0.4732	0.2724	0.5083	1.0000	0.1198	0.3366	0.2252	0.5550
	(64)	(64)	(64)	(64)	(64)	(63)	(63)	(65)	(65)	(65)	(65)	(65)	(64)	(64)	(58)
	P=0.001	P=0.483	P=0.000	P=0.158	P=0.000	P=0.227	P=0.476	P=0.000	P=0.014	P=0.000	P=*****	P=0.171	P=0.003	P=0.037	P=0.000
CD	0.2029	0.2741	0.0920	0.2601	0.0895	0.0160	0.4806	0.2337	0.0507	0.1825	0.1198	1.0000	0.1529	0.0124	0.1030
	(64)	(64)	(64)	(64)	(64)	(63)	(63)	(65)	(65)	(65)	(65)	(65)	(64)	(64)	(58)
	P=0.054	P=0.014	P=0.235	P=0.019	P=0.241	P=0.450	P=0.000	P=0.030	P=0.344	P=0.073	P=0.171	P=*****	P=0.114	P=0.461	P=0.221
DUST	0.4625	0.3713	0.4271	0.6429	0.3104	0.2063	0.0817	0.7530	0.1419	0.3298	0.3366	0.1529	1.0000	0.0392	0.2487
	(63)	(63)	(63)	(63)	(63)	(62)	(62)	(64)	(64)	(64)	(64)	(64)	(64)	(63)	(57)
	P=0.000	P=0.001	P=0.000	P=0.000	P=0.007	P=0.054	P=0.264	P=0.000	P=0.132	P=0.004	P=0.003	P=0.114	P=*****	P=0.322	P=0.031
RAIN	0.0677	-0.0204	0.4202	0.1156	0.0070	0.1331	0.1804	-0.0443	0.3694	0.0966	0.2252	0.0124	0.0592	1.0000	-0.0052
	(63)	(63)	(63)	(63)	(63)	(63)	(63)	(64)	(64)	(64)	(64)	(64)	(63)	(64)	(58)
	P=0.299	P=0.437	P=0.000	P=0.184	P=0.478	P=0.149	P=0.079	P=0.364	P=0.001	P=0.224	P=0.037	P=0.461	P=0.322	P=*****	P=0.485
F	0.6575	0.0598	0.4607	0.2435	0.8923	0.2643	0.2099	0.6018	0.2218	0.8212	0.5550	0.1030	0.2487	-0.0052	1.0000
	(57)	(57)	(57)	(57)	(57)	(58)	(58)	(58)	(58)	(58)	(58)	(58)	(57)	(58)	(58)
	P=0.000	P=0.329	P=0.000	P=0.034	P=0.000	P=0.022	P=0.057	P=0.000	P=0.047	P=0.000	P=0.000	P=0.221	P=0.031	P=0.485	P=*****

(COEFFICIENT / (CASES) / SIGNIFICANCE) (A VALUE OF 99.0000 IS PRINTED IF A COEFFICIENT CANNOT BE COMPUTED)

Table 5.24. Pearson correlation matrix for various variables for Winter 1983.

----------PEARSON CORRELATION COEFFICIENTS----------

	AL	MNI	FE	ZNI	NI	MNS	ZNS	CU	PB	CO	CR	CD	DUST	RAIN	F
AL	1.0000	0.1127	0.7440	0.5033	0.8336	0.2353	0.1437	0.8658	0.3208	0.8517	0.6063	0.1505	0.5111	0.3662	0.8353
	(71)	(71)	(71)	(71)	(71)	(67)	(67)	(71)	(71)	(71)	(71)	(71)	(71)	(70)	(68)
	P=*****	P=0.175	P=0.000	P=0.000	P=0.000	P=0.028	P=0.123	P=0.000	P=0.003	P=0.000	P=0.000	P=0.105	P=0.000	P=0.001	P=0.000
MNI	0.1127	1.0000	0.0817	0.0891	0.0355	0.5324	-0.0604	0.1320	-0.0169	0.3534	0.0720	-0.0799	0.0678	-0.2012	0.0343
	(71)	(71)	(71)	(71)	(71)	(67)	(67)	(71)	(71)	(71)	(71)	(71)	(71)	(70)	(68)
	P=0.175	P=*****	P=0.249	P=0.230	P=0.384	P=0.000	P=0.314	P=0.136	P=0.444	P=0.001	P=0.275	P=0.254	P=0.287	P=0.047	P=0.391
FE	0.7440	0.0817	1.0000	0.4145	0.6045	0.2987	0.1781	0.7303	0.2499	0.7931	0.4812	0.0446	0.5133	0.3902	0.6095
	(71)	(71)	(71)	(71)	(71)	(67)	(67)	(71)	(71)	(71)	(71)	(71)	(71)	(70)	(68)
	P=0.000	P=0.249	P=*****	P=0.000	P=0.000	P=0.007	P=0.075	P=0.000	P=0.018	P=0.000	P=0.000	P=0.356	P=0.000	P=0.000	P=0.000
ZNI	0.5033	0.0891	0.4145	1.0000	0.4335	0.0795	0.3409	0.5990	-0.0614	0.4763	0.4952	0.2135	0.7168	0.2245	0.4239
	(71)	(71)	(71)	(71)	(71)	(67)	(67)	(71)	(71)	(71)	(71)	(71)	(71)	(70)	(68)
	P=0.000	P=0.230	P=0.000	P=*****	P=0.000	P=0.261	P=0.002	P=0.000	P=0.305	P=0.000	P=0.000	P=0.037	P=0.000	P=0.031	P=0.000
NI	0.8336	0.0355	0.6045	0.4335	1.0000	-0.0257	0.1657	0.7574	0.1301	0.8010	0.6321	0.1640	0.2533	0.2684	0.9723
	(71)	(71)	(71)	(71)	(71)	(67)	(67)	(71)	(71)	(71)	(71)	(71)	(71)	(70)	(68)
	P=0.000	P=0.384	P=0.000	P=0.000	P=*****	P=0.418	P=0.090	P=0.000	P=0.140	P=0.000	P=0.000	P=0.086	P=0.017	P=0.012	P=0.000
MNS	0.2353	0.5324	0.2987	0.0795	-0.0257	1.0000	0.0066	0.1890	0.1628	0.2293	0.0703	-0.0975	0.2059	0.1525	-0.0131
	(67)	(67)	(67)	(67)	(67)	(67)	(67)	(67)	(67)	(67)	(67)	(67)	(67)	(67)	(65)
	P=0.028	P=0.000	P=0.007	P=0.261	P=0.418	P=*****	P=0.479	P=0.063	P=0.094	P=0.031	P=0.286	P=0.216	P=0.047	P=0.109	P=0.459
ZNS	0.1437	-0.0604	0.1781	0.3409	0.1657	0.0066	1.0000	0.2228	-0.0829	0.1781	0.1995	0.4084	0.2008	0.4031	0.2408
	(67)	(67)	(67)	(67)	(67)	(67)	(67)	(67)	(67)	(67)	(67)	(67)	(67)	(67)	(65)
	P=0.123	P=0.314	P=0.075	P=0.002	P=0.090	P=0.479	P=*****	P=0.035	P=0.253	P=0.075	P=0.053	P=0.000	P=0.052	P=0.000	P=0.027
CU	0.8658	0.1320	0.7303	0.5990	0.7574	0.1890	0.2228	1.0000	0.2699	0.8217	0.6156	0.2543	0.6679	0.4439	0.7981
	(71)	(71)	(71)	(71)	(71)	(67)	(67)	(71)	(71)	(71)	(71)	(71)	(71)	(70)	(68)
	P=0.000	P=0.136	P=0.000	P=0.000	P=0.000	P=0.063	P=0.035	P=*****	P=0.011	P=0.000	P=0.000	P=0.016	P=0.000	P=0.000	P=0.000
PB	0.3208	-0.0169	0.2499	-0.0614	0.1301	0.1628	-0.0829	0.2699	1.0000	0.1966	0.0771	-0.1637	0.1017	0.3645	0.1688
	(71)	(71)	(71)	(71)	(71)	(67)	(67)	(71)	(71)	(71)	(71)	(71)	(71)	(70)	(68)
	P=0.003	P=0.444	P=0.018	P=0.305	P=0.140	P=0.094	P=0.253	P=0.011	P=*****	P=0.050	P=0.261	P=0.086	P=0.199	P=0.001	P=0.084
CO	0.8517	0.3534	0.7931	0.4763	0.8010	0.2293	0.1781	0.8217	0.1966	1.0000	0.5925	0.1463	0.4539	0.2582	0.7943
	(71)	(71)	(71)	(71)	(71)	(67)	(67)	(71)	(71)	(71)	(71)	(71)	(71)	(70)	(68)
	P=0.000	P=0.001	P=0.000	P=0.000	P=0.000	P=0.031	P=0.075	P=0.000	P=0.050	P=*****	P=0.000	P=0.112	P=0.000	P=0.015	P=0.000
CR	0.6063	0.0720	0.4812	0.4952	0.6321	0.0703	0.1995	0.6156	0.0771	0.5925	1.0000	0.1364	0.4863	0.2321	0.5905
	(71)	(71)	(71)	(71)	(71)	(67)	(67)	(71)	(71)	(71)	(71)	(71)	(71)	(70)	(68)
	P=0.000	P=0.275	P=0.000	P=0.000	P=0.000	P=0.286	P=0.053	P=0.000	P=0.261	P=0.000	P=*****	P=0.128	P=0.000	P=0.027	P=0.000
CD	0.1505	-0.0799	0.0446	0.2135	0.1640	-0.0975	0.4084	0.2543	-0.1637	0.1463	0.1364	1.0000	0.1352	0.1015	0.1757
	(71)	(71)	(71)	(71)	(71)	(67)	(67)	(71)	(71)	(71)	(71)	(71)	(71)	(70)	(68)
	P=0.105	P=0.254	P=0.356	P=0.037	P=0.086	P=0.216	P=0.000	P=0.016	P=0.086	P=0.112	P=0.128	P=*****	P=0.130	P=0.202	P=0.076
DUST	0.5111	0.0678	0.5133	0.7168	0.2533	0.2059	0.2008	0.6679	0.1017	0.4539	0.4863	0.1352	1.0000	0.2803	0.2783
	(71)	(71)	(71)	(71)	(71)	(67)	(67)	(71)	(71)	(71)	(71)	(71)	(71)	(70)	(68)
	P=0.000	P=0.287	P=0.000	P=0.000	P=0.017	P=0.047	P=0.052	P=0.000	P=0.199	P=0.000	P=0.000	P=0.130	P=*****	P=0.009	P=0.011
RAIN	0.3662	-0.2012	0.3902	0.2245	0.2684	0.1525	0.4031	0.4439	0.3645	0.2582	0.2321	0.1015	0.2803	1.0000	0.3637
	(70)	(70)	(70)	(70)	(70)	(67)	(67)	(70)	(70)	(70)	(70)	(70)	(70)	(70)	(68)
	P=0.001	P=0.047	P=0.000	P=0.031	P=0.012	P=0.109	P=0.000	P=0.000	P=0.001	P=0.015	P=0.027	P=0.202	P=0.009	P=*****	P=0.001
F	0.8353	0.0343	0.6095	0.4239	0.9723	-0.0131	0.2408	0.7981	0.1688	0.7943	0.5905	0.1757	0.2783	0.3637	1.0000
	(68)	(68)	(68)	(68)	(68)	(65)	(65)	(68)	(68)	(68)	(68)	(68)	(68)	(68)	(68)
	P=0.000	P=0.391	P=0.000	P=0.000	P=0.000	P=0.459	P=0.027	P=0.000	P=0.084	P=0.000	P=0.000	P=0.076	P=0.011	P=0.001	P=*****

(COEFFICIENT / (CASES) / SIGNIFICANCE) (A VALUE OF 99.0000 IS PRINTED IF A COEFFICIENT CANNOT BE COMPUTED)

As shown in Tables 5.20, Al was found significantly correlated with F ($p=0.003$) and insoluble Mn (MnI) and Fe ($p<0.001$) annually, though the correlation coefficients (r) are rather low (0.48 for F, 0.35 for insoluble Mn, and 0.56 for Fe). This indicates that Al and F might not be entirely coming from the same source, and also that Comalco may not be the only source of Al, while Temco may not be the only source of insoluble Mn and Fe. Additionally, Al is also significantly correlated with many other trace metals including insoluble Zn (ZNI), Ni, Cu, Co, and Cr, as well as the total insoluble dust (all with $p < 0.001$) annually, and the correlation coefficients were found better for Ni, Cu, and Co, with $r=0.70$, 0.65, and 0.68 respectively. This suggests a fairly strong linear relationship between Al and these trace metals.

Apart from the positive correlation with Al, F is also significantly correlated with Ni ($r=0.70$), Cu ($r=0.47$) and Co ($r=0.57$), all at significance levels <0.001. Thus, it is possible that some of the Al, F, Ni, Cu, and Co could well be contributed by the same source, presumably the aluminium smelter. Perhaps this explains why the distribution patterns of these elements bear some similarities, as shown in Figures 5.5, 5.6, 5.9, and 5.10 (the spatial distribution for Co is not given). Unlike Al, F is not significantly correlated with Mn (both soluble and insoluble) or Fe. Thus, it is the best tracer for the emissions of the aluminium smelter in the lower Tamar Valley.

The deposition of F appears to be more affected by the rainfall than that of Al, probably due to the fact that a substantial proportion of this element has originated from submicron aerosol particles, hence its deposition depends largely on the processes of rainout and washout.

Seasonally, Al and F correlated best in winter, with $r=0.83$ at $p<0.001$ (Table 5.24). This was followed by autumn, with $r>0.65$ at the same significance level (Tables 5.23). That Al and F correlated better in colder months confirms the analysis in Section 5.5.

The correlation between Al and Fe was least significant in summer, with $r<0.07$ at $p=0.32$ (Tables 5.22). Al also correlates best with Ni, Cu, and Co in winter, with r for each of these element greater than 0.83 at $p<0.001$ (Table 5.24). On the other hand, Al and Fe correlate best in summer, with $r=0.76$ at $p<0.001$ (Tables 5.22). Al had a better correlation with the insoluble Mn in autumn, with $r=0.61$ at $p<0.001$

(Table 5.23).

F also correlates best with Ni, Cu in winter, and Co in autumn, with r=0.97, 0.80 and 0.82 respectively at p<0.001 for all cases.

Annually, the insoluble Mn is significantly correlated with Fe (p=0.003), insoluble Zn (ZNI) (p=0.007), soluble Mn (MNS), Cu, Co, and the total insoluble dust (p<0.001 for all cases). If Mn is used as a tracer of air emissions from Temco, then the deposition of some of these correlated trace metals must also have come from the same source. Unlike Al and F, Mn (both soluble and insoluble) is not significantly correlated with Ni (Table 5.20)

Fe is significantly correlated with all other insoluble trace elements. This indicates the widespread distribution of this metal in the ambient air environment.

Seasonally, the insoluble Mn and soluble Mn are significantly correlated in autumn (p=0.003) and winter (p<0.001), but not in spring (p=0.085) and summer (p=0.337). This is not unexpected in view of the higher rainfall during the colder months. While insoluble Mn and Fe are only significantly correlated in autumn (p<0.001), soluble Mn and Fe are significantly correlated in both autumn (p<0.001) and winter (p=0.007).

It is interesting to include Pb, a well known major emission from motor vehicles, for comparison. Annually, Pb is not significantly correlated with Al (p=0.062), F (p=0.369), insoluble Mn (p=0.365), soluble Mn (p=0.116), and Ni (p=0.213), but significantly correlated with Fe, insoluble Zn, Cr, Cd (with p all <0.001), Cu (p=0.005) and Co (p=0.001). This virtually rules out that the two heavy industries are the major sources of Pb, and the deposition of some Fe, insoluble Zn, Cr, Cd, Cu, and Co could have been caused by traffic.

Using the same set of data, the Spearman rank-order correlation coefficient, r_s, is also computed using the subprogram NONPAR CORR in SPSS. Unlike Pearson correlation, Spearman correlation is non-parametric, i.e. it does not depend upon a normal distribution or the metric quality of interval scales, but the computation requires the use of rankings, rather than the absolute values of variables (Nie et al., 1975).

5.6.3 Correlations Between Al and F Within and Outside 3 km of Comalco

Table 5.25 gives the means and standard deviations of Al and F, as well as the Pearson correlation coefficients between the two elements for all samples within and outside 3 km of Comalco for all directions. The number of samples within and outside 3 km of Comalco were about the same.

Table 5.25. Correlations between Al and F within and outside 3 km.

Element		Distance		Type of Funnel	
		3 km	> 3 km	Glass	Plastic
Al	Mean	3491.4	885.7	4015.8	4716.4
	No. of cases	115	119	37	36
	Std. Dev.	3436.7	1241.8	3202.3	4606.8
F	Mean	4220.3	383.6	4847.6	5252.8
	No. of cases	108	110	34	33
	Std. Dev.	7424.3	494.2	6104.3	6374.4
Pearson r		0.4117 (106) p<0.001	0.0647 (110) p=0.251	0.8028 (33) p<0.001	0.4113 (32) p=0.001

The mean deposition rates of Al and F for all samples within 3 km were about 4 and 11 times the rates of those outside 3 km. This indicates the high deposition rates within 3 km of the aluminium smelter. Al and F are significantly correlated for samples collected within 3 km of Comalco but not for samples collected outside the distance (p=0.251). This could be due to the different deposition patterns between Al and F after a distance of 3 km, as shown in Figure 5.3, or due to some other sources which also contributed to the depositions of Al or F.

5.6.4 Correlations Between Al and F in Glass and Plastic Gauges

Deposition samples duplicated by plastic deposit gauges were also tested statistically for the correlations between Al and F. The results are also given in Table 5.25. The plastic gauges appear to be more effective so far as the collection of the depositions of Al and F were concerned. They collected about 17% and 8% more Al and F respectively

than the glass deposit gauges. However, the standard deviations for the depositions of Al And F in plastic gauges are also higher than those in glass gauges. Thus, the variations observed between the collection efficiencies of these two types of gauges for Al and F could be due to the sampling fluctuations. More data are needed for further statistical analysis before any conclusion can be drawn on the collection efficiency of either gauge.

Al and F are significantly correlated in both glass and plastic deposit gauges, though much better correlation coefficient is found for the glass gauges (r=0.80). This could be due to the smaller sampling fluctuations (as indicated by the smaller standard deviations) of Al and F in glass gauges.

5.7 Trace Metals Measurements by the Department of the Environment

Chemical analyses on the four deposition or dust fallout samples collected monthly by the Tasmanian Department of the Environment in conjunction with the HEC in the lower Tamar Valley did not start until after the commencement of this study, even though heavy metals have been analysed in similar samples collected in other parts of the State. The results for 1982-83 (year ended at June) as reported by the Department of the Environment are given in Table 5.26. Only the insoluble trace metals are measured.

Table 5.26. Heavy metals in dust fallout in the lower Tamar Valley for 1982-83 as reported by the Department of the Environment. The levels are expressed as $\mu g\ m^{-2}\ day^{-1}$.

Location	Cd	Cu	Zn	Pb	Cr	Mn	Fe	Co	Ni
Kayena	0.1	9	16	2	0.4	58	300	0.6	1
Anne St.	0.2	6	47	6	1.1	305	500	0.7	5
HEC Station	5.5	18	297	15	2.1	224	800	2.4	15
Reservoir	0.4	11	91	5	0.8	71	500	0.5	6

The level of Mn was highest at the sampling location in Anne Street (George Town), followed by the sampling location at the HEC substation, which is about 1.2 km ESE of Comalco. The sampling location at the HEC

substation had the highest levels of other heavy metals, particularly Fe (800 μg m^{-2} day^{-1}) and Zn (297 μg m^{-2} day^{-1}).

Two of the above sampling locations (i.e. those at Anne Street and the HEC substation) were close to locations 11 and 5 respectively in this study. It was found that the levels of Mn and Fe at the HEC substation location were the same order of magnitude as those at location 5, though the level of Zn was about 7 times higher (Table 5.9). On the other hand, the levels of Mn and Fe at Anne Street were about one third of those at location 11 (Table 5.6).

It should be noted that the results obtained by the Department of the Environment and those obtained by this study may not be entirely comparable for reasons already discussed in Section 5.3 (see page 308-309).

The levels of heavy metals at the same locations in 1983-84 as reported by the Department of the Environment were comparable to those in 1982-83 (Table 5.27), though the levels of Mn appeared to be slightly higher at Kayena, Anne Street and the HEC substation.

Table 5.27. Heavy metals in dust fallout for 1983-84 in the lower Tamar Valley as reported by the Department of the Environment. The levels are expressed as μg m^{-2} day^{-1}.

Location	Cd	Cu	Zn	Pb	Cr	Mn	Fe	Co	Ni
Kayena	-	12	14	3	-	81	220	-	0.3
Anne St.	0.1	1	26	2	0.1	360	300	0.2	6.7
HEC	1.8	32	247	11	0.1	244	860	0.7	9.9
Reservoir	0.1	0.2	5	2	-	27	650	0.3	0.7

No analyses of Al and F in the dust fallout samples were undertaken by the Department of the Environment, even though they are two of the major air emissions from the alumunium smelter.

5.8 Comparison with Fluoride Deposition as Monitored by Comalco

Comalco has monitored fluoride, both in vegetation and precipitation, as part of their environmental programmes. Surveys of fluoride levels in vegetation have been carried out in the Tamar Valley

and surrounding bushland since 1957, while the collection and analysis of bulk (wet and dry) deposition samples for fluoride were started in 1975 (Lee, 1982). Table 5.28 shows the levels of fluoride in the deposition samples, which were collected in plastic deposit gauges placed at a height of 4 m above the ground, for 25 sampling locations in 1983. The data were obtained from Comalco.

The annual average of F deposition as monitored by Comalco in 1983 varied from 322 $\mu g\ m^{-2}\ day^{-1}$ at location 20 to 41 466 $\mu g\ m^{-2}\ day^{-1}$ at location 6, which are 13.2 km SSE and 0.3 km ENE of the aluminium smelter respectively. Over 4800, 2000, and 1000 $\mu g\ m^{-2}\ day^{-1}$ of F were recorded at locations within 1 km, 1 to 2 km, and 2 to 4 km of the smelter respectively. A range of 328 -366 $\mu g\ m^{-2}\ day^{-1}$ was found at the so-called "control" sites.

Some monitoring locations of this study were close to those of Comalco (the distances between them varied from a few metres to a few hundred metres), as given in Table 5.29. Comparisons of the fluoride levels at these locations obtained by both studies from January to August 1983 show that very few values actually agreed with each other. This is to be expected because even duplicated samples were found to produce different levels, as discussed earlier. However, quite a few values were comparable to each other within the order of magnitude. The F levels obtained in this study were consistently higher than those obtained by Comalco in January and February for all available compared locations. The reverse is true for other months with a few exceptions. For example, location 17 of this study consistently recorded much higher (about 14 times in January and June) F levels than location 11 of Comalco, even though they were a few hundred metres apart, with location 17 of this study slightly closer to Comalco.

The differences in the deposition rates of F as monitored in this study and Comalco at locations close to each other could be caused by many factors: the actual locality of the deposit gauges; the differences in sampling (plastic gauges are used by Comalco and they are placed at different heights from this study) and analytical procedures (a more concentrated buffer TISAB is used by Comalco, and the time for each measurement is about 5 minutes, as compared to at least 30 minutes in this study). Most importantly, the complexity of the atmospheric

Table 5.28. Deposition of soluble F as monitored by Comalco in 1983 at 25 sampling locations.

LOCATION	DISTANCE/ DIRECTION FROM SMELTER (KMS)		1983 - mg $F^-/m^2/day$ JAN.	FEB.	MAR.	APR.	MAY	JUN.	JULY	AUG.	SEPT.	OCT.	NOV.	DEC.	AV.
1	7.2	ESE	0.321	0.287	1.027	0.187	0.751	0.793	0.879	0.621	1.204	0.544	0.570	0.233	0.618
2	5.8	ESE	0.434	-	1.215	0.881	0.491	0.801	3.970	0.617	0.884	0.434	0.416	0.253	0.945
3	3.5	ESE	0.859	-	1.843	1.324	1.007	1.137	1.125	0.921	1.487	0.624	0.632	0.285	1.022
4	2.5	ESE	-	-	4.473	1.899	-	1.717	1.791	2.213	2.389	1.141	1.001	0.764	1.932
5	1.8	ESE	2.286	-	3.879	4.228	5.217	4.345	2.770	-	2.360	0.806	-	1.257	3.016
6	0.3	E	9.446	-	72.73	55.870	53.243	48.749	48.026	33.959	74.958	25.571	23.885	9.691	41.466
7	0.5	NNE	-	-	7.440	4.843	1.952	2.638	3.699	1.346	3.168	6.166	1.322	2.842	3.542
8	0.8	NNW	3.005	-	13.473	-	5.972	3.170	1.005	1.564	3.834	5.691	7.980	2.380	4.807
9	2.0	NW	-	-	7.235	-	2.787	2.282	1.963	-	3.290	1.156	-	1.841	2.936
10	0.3	WSW	4.358	-	12.598	19.985	7.935	7.054	5.683	12.994	13.030	3.822	2.718	6.798	8.816
11	1.2	ENE	4.096	-	4.480	6.205	-	1.109	-	1.639	3.955	1.983	1.421	2.435	3.036
12	1.3	ENE	-	-	-	0.638	1.018	0.790	1.205	0.629	1.443	0.656	0.255	0.915	0.839
13	1.3	NNE	0.483	-	-	-	0.361	1.975	0.561	0.564	0.649	1.397	0.681	1.095	0.862
14	1.4	WSW	0.474	-	1.865	-	0.873	3.462	1.109	0.884	0.504	0.482	2.292	0.603	1.255
15	0.5	SSW	1.101	-	-	5.555	1.621	1.452	1.176	3.617	4.103	1.184	0.475	2.331	2.262
16	3.3	E	0.897	-	1.526	1.392	1.221	0.554	0.953	0.987	1.471	0.563	0.493	0.646	0.973
17	6.5	NW	-	-	0.987	0.535	0.773	0.459	0.531	0.275	0.514	0.223	0.187	0.314	0.480
18	2.9	WSW	0.392	-	0.886	0.601	0.625	-	0.664	0.402	0.414	0.333	0.447	0.361	0.513
19	4.9	WNW	0.223	-	0.636	0.478	0.352	0.338	0.510	-	0.376	0.203	0.191	0.212	0.352
20	13.2	SSE	0.184	0.108	0.686	0.459	0.303	0.540	0.430	0.154	0.426	0.146	0.223	0.202	0.322
21	8.8	SSE	0.182	0.059	0.651	0.383	0.585	0.495	0.393	0.165	0.666	0.142	0.260	0.194	0.348
22	10.5	SE	0.282	0.049	0.903	0.589	0.327	0.672	0.491	0.351	0.609	0.234	0.290	0.263	0.422
23	5.4	WSW	0.350	0.144	0.682	0.525	-	-	-	0.297	0.399	0.197	0.401	0.026	0.336
24	5.2	NW	0.202	-	1.321	1.311	0.809	0.903	1.087	0.584	0.655	0.330	0.213	0.313	0.703
GUEST 25 LODGE	4.2	W	0.243	-	0.788	0.344	0.311	0.680	0.429	0.200	0.452	0.192	-	0.437	0.408
AVERAGE MONTHLY VALUES			1.491	0.129* 0.026**	6.424	5.154	4.024	3.744	3.498	2.954	4.930	2.169	2.107	1.468	
LAUNCESTON			0.697	-	0.560	0.372	0.187	0.428	0.141	0.167	0.413	0.198	0.200	0.246	0.328
LEBRINA			0.158	0.085	0.548	0.346	0.696	0.640	0.429	0.279	0.363	0.313	0.338	0.201	0.366
BEECHFORD			0.083	0.148	1.043	0.435	0.164	-	0.250	0.517	0.437	0.184	0.293	0.059	0.328
AVERAGE MONTHLY VALUES			0.313	0.117	0.717	0.384	0.349	0.534	0.273	0.321	0.404	0.232	0.277	0.169	

* FOR 5 PTS ** FOR 25 PTS

Table 5.29. Comparison of fluoride levels ($\mu g\ m^{-2}\ day^{-1}$) in precipitation obtained by this study and Comalco.

	Location									
Comalco	1	3	4	5	9	11	12	14	19	23
This Study	2	3	4	5	9	17	6	7	11	13
January	409	859	-	2286	-	4096	-	474	321	350
	741	1398	2907	7379	-	58544	2650	1272	685	721
February	287	-	-	-	-	-	-	-	-	-
	487	-	-	-	-	-	-	-	-	-
March	1027	1843	4473	3879	7235	4480	-	1865	636	682
	278	302	482	1513	-	7948	465	1261	373	1664
April	187	1324	1899	4228	-	6205	638	-	478	525
	417	725	1085	1302	4488	7376	91	832	282	165
May	751	1007	-	5217	2787	-	1018	873	352	-
	504	593	1001	2941	2769	12122	891	1061	363	284
June	793	1137	1717	4345	2282	1109	790	3462	338	-
	-	484	850	-	4211	15823	-	1877	345	134
July	879	1125	1791	2770	1963	-	1205	1109	510	-
	586	589	1012	1492	2636	6130	673	-	399	221
August	621	921	2213	-	-	1639	629	884	-	297
	311	619	954	2043	1654	5731	388	550	184	265

transport makes it very difficult to reproduce results even though two deposit gauges were placed side by side. This is illustrated by the results obtained at location 17 where four deposit gauges (two glass and two plastic) were placed together, as shown in Table 5.5. While the deposition of F in the two glass deposit gauges (17 and 17B) agreed within 13%, the difference of deposition of F in the two plastic deposit gauges (17C and 17D) was as high as 61%.

5.9 Sampling and Analyses of Precipitation

In the past two decades, 'acid rain' has attracted a lot of attention and publicity by scientists and the general public, especially in North America and Europe where the rain has become more acidic presumably as a result of anthropogenic inputs of SO_x and NO_x to the atmosphere and their conversion to H_2SO_4 and HNO_3. Hence, the interest in the chemical composition of precipitation has grown tremendously because of its environmental consequences (Ridder et al., 1985).

The chemical composition of precipitation is the product of a complex series of processes (Hidy and Countess, 1984). A study of the chemical composition of precipitation can give insight not only into the composition of atmospheric trace gases and aerosols which are scavenged by water droplets during the formation of cloud and precipitation, but also into some important chemical inter-conversion processes, as well as parts of the biogeochemical cycles of most elements (Francey, 1984). Thus, one of the objectives of this study was to analyse the chemical composition, particularly the acidity of the monthly bulk deposition samples, which include wet (the precipitation) as well as the dry deposition.

5.9.1 Acidity of the Deposition Samples

As described in Section 3.6.1 (page 79), the pH of the monthly bulk deposition samples was measured soon after collection (normally within 2 days) and before the samples were filtered. A sample is defined as being acidic if its pH is less than 5.6, the pH of 'normal, unpolluted rain' (USEPA, 1979). It should be realised that this reference was assigned for convenience, and not because it has intrinsic meaning as a global 'background level' (Graedel et al., 1982), as recent studies (Sequeira, 1982) have shown that there is wide variability in natural acidity.

The results of pH measurements from July 1982 to August 1983 are shown in Table 5.30. Only the samples collected in glass deposit gauges are considered. It must be noted that the pH measured is the net 'acidity' which is a function of locality and is determined by the acidic and basic components in the bulk samples. For example, alkaline substances such as NH_3 and $CaCO_3$ are able to neutralize some acidic

Table 5.30. pH of monthly deposition samples in the lower Tamar Valley, July 1982 - August 1983.

Year	1982						1983								Total Samples	pH<5.6	pH<5.0
Location	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug			
1	6.6	7.0	5.2	5.5	5.8	5.7	6.0	4.5	*	5.8	5.4	5.2	5.5	5.4	13	7	1
2	*	6.4	6.9	5.8	6.5	5.2	5.6	7.5	*	4.6	6.5	6.3	7.0	6.6	12	2	1
3	5.6	6.5	5.7	5.9	5.0	5.4	5.0	7.6	4.9	4.6	5.3	5.7	6.2	6.9	14	6	4
4	5.4	5.0	5.0	5.7	5.5	5.4	5.6	7.5	4.4	6.0	5.2	4.8	5.1	4.7	14	10	5
5	4.6	6.2	4.8	*	7.7	5.9	*	6.9	4.3	5.8	*	6.8	5.9	6.9	9	3	3
6	5.4	6.7	6.4	5.7	4.7	4.7	5.1	7.1	4.3	5.1	6.8	6.8	6.8	7.3	14	6	3
7	5.5	*	7.0	6.1	6.5	*	*	*	*	*	*	*	*	*	4	1	0
8	6.5	6.0	6.2	*	*	*	5.5	6.2	5.3	*	*	*	*	5.7	7	2	0
9	5.4	7.1	6.7	-	7.0	6.1	6.4	7.4	*	*	*	7.0	*	7.1	7	1	0
10	6.5	5.0	6.4	-	6.4	5.5	5.9	7.6	5.7	5.0	5.3	5.1	5.8	6.1	13	5	2
11	6.3	6.5	6.3	6.6	7.3	*	6.4	7.7	6.1	6.5	6.4	6.4	6.5	5.8	13	0	0
12	6.4	6.6	7.8	*	*	*	6.0	7.2	5.3	6.5	5.6	5.6	6.4	5.3	12	2	0
13	6.4	6.8	6.4	6.1	6.4	6.2	6.4	7.6	5.8	5.4	5.8	5.8	6.2	6.0	14	0	0
14	4.0	7.2	5.7	6.2	6.1	6.3	6.1	7.1	5.2	4.6	4.9	5.2	6.0	4.9	14	6	4
15	5.7	6.1	5.7	6.7	*	7.8	5.0	7.4	6.1	5.4	5.8	6.3	5.3	5.5	12	4	1
16	6.1	6.5	6.4	5.6	5.1	6.2	7.0	4.7	5.3	5.4	6.4	6.3	6.1	5.3	14	5	1
17+	-	-	-	-	-	5.6	5.8	6.7	5.5	6.3	*	6.0	6.7	7.0	8	1	0
Total	15	14	16	11	12	11	15	16	13	14	12	15	14	16	194	61	25
pH<5.6	6	2	3	1	4	5	4	2	8	7	5	4	3	6			
pH<5.0	2	2	2	0	2	1	2	2	4	4	1	1	0	2			
Min. pH	4.0	5.0	4.8	5.5	4.7	4.7	5.0	4.5	4.2	4.6	4.9	4.8	5.1	4.7			
Max. pH	6.6	7.2	7.8	6.7	8.0	6.3	7.0	7.7	6.1	6.5	6.5	7.0	7.0	7.3			

+ Average of samples 17 and 17A.
* Contaminated with bird droppings or algae.
- Sample damaged.

species found in precipitation (Asman and Jonker, 1982). The net effect of the dry deposition component in the bulk sample upon the measured pH is difficult to quantify, as it depends on geographical, temporal and meteorological factors (Hansen and Hidy, 1982). As the dry deposition is mainly contributed by the larger alkaline species such as Ca^{2+}, Mg^{2+} and K^{+}, Na^{+} rather than the acidic aerosol particles containing SO_4^{2-} and NO_3^{-}, it is probable that the pH of bulk deposition samples could be higher than that of concurrently collected wet-only samples (Hansen and Hidy, 1982). Studies by Galloway and Likens (1976), Parkhust et al. (1980), and Popp et al. (1984) appear to support this conclusion. Additionally, the sea spray in the setting of the lower Tamar Valley would also tend to enhance the pH. Thus, the following discussion must be viewed in this perspective.

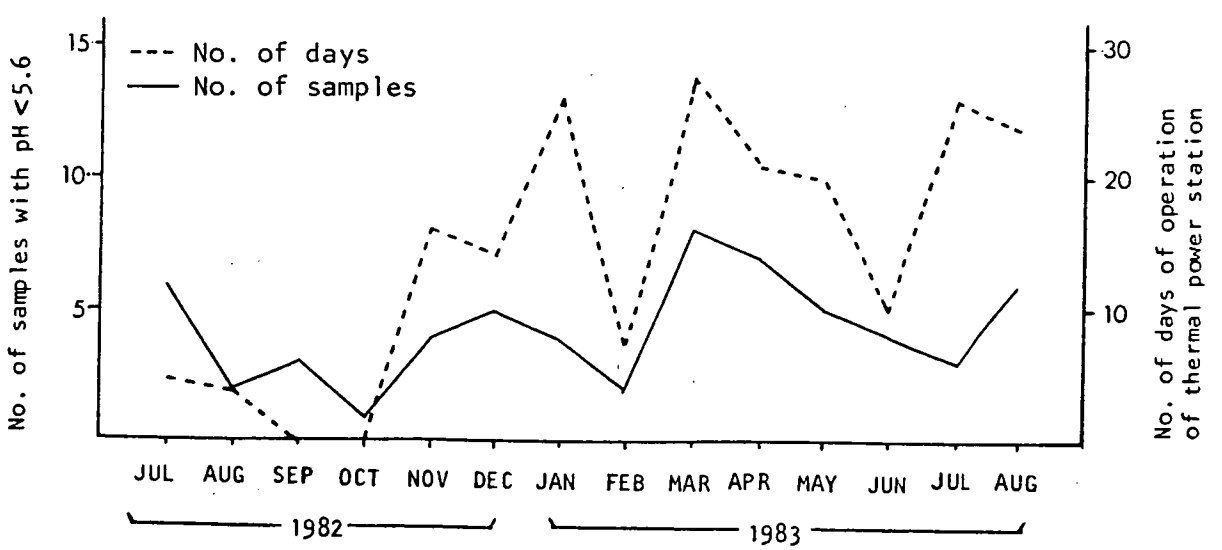
The pH of the monthly bulk deposition samples varied from location to location, and ranged from 4.0 to 8.0. For 61 out of 194 samples (or 31.4%) measured, the pH was < 5.6. Of these, 25 samples (or 12.9%) had pH < 5.0. These figures are obtained excluding the contaminated (due to bird dropping or algae which could be detected visually) or damaged samples.

It appears that the locations along NW (4, 6, 10) and SE (3, 16) of the thermal power station had higher frequency of collecting acidic samples. Of these, location 4, about 1 km NW of the power station and 3 km SE of the industrial area, collected the highest number of acidic samples (10 out of 14). Location 1, about 7 km W of the power station, and over the other side of the Tippogoree Hills, had the second highest number of acidic samples (7 out of 13). It was highly likely that the air emissions from the 107 m stack of the power station were transported by the fresh to strong westerly airstreams before rainout or washout at the location. The diurnal variations of the westerly winds, as recorded at a location about 3 km NW of the power station, were greatest in summer (the frequency of occurrence varying from a minimum of 7% at noon to a maximum of 25% at 2100 hours), and smallest in winter (the frequency of occurrence varying from a minimum of 13% at 0600 hours to a maximum of 19% at 1800 hours) (Low, 1985b). All winter month samples in 1983 at location 1 were acidic. Location 14, 5.2 km SW of the power station, was generally less influenced by the air emissions from Comalco and Temco, as

evidenced by the relatively low mean deposition rates of Al, F, Mn and Fe. However, 6 out of 14 samples collected at this location were acidic. Of these, four had pH < 5.0, including the lowest pH (4.0) measured in the lower Tamar Valley. This could have resulted from the transport of the air emissions from the power station by the NE katabatic winds originating from the Tippogoree Hills. Indeed, all acidic samples at location 14 were collected in colder months when katabatic winds are most frequent.

Most samples collected near Comalco or Temco (locations 7, 8, 9 and 17) had higher pH. This could be due to the presence of more alkaline species contributed by the two heavy industries and the concrete mixing plant (e.g. Ca^{2+}, Mg^{2+} etc.). The major acidic species in the lower Tamar Valley are believed to be SO_4^{2-}, NO_3^- and F^-. It is also possible that some SO_4^{2-} was of marine origin. While both Comalco and Temco are operating 24 hours a day throughout the year, the thermal power station is only operated intermittently. Thus it may be possible to correlate the number of days of the operation of the power station with the number of acidic samples collected. Figure 5.14 shows that the general trends between the two parameters are similar. The number of acidic samples collected in September and October, 1982, were due to other industrial sources as the thermal power station was not operated during these two months.

Figure 5.14. Correlation of the acidic samples with the operation of the thermal power station.



5.9.2 Acidic Species in the Deposition Samples

Although pH gives the acidity of the precipitation samples, it does not indicate the acid-base systems responsible for the observed free acidity, and a variety of components such as inorganic or organic, weak or strong acids, or metal oxides (e.g. those of Al or Fe) may contribute to the free acidity of rain (Delmas and Gravenhorst, 1983). In order to investigate the concentrations of the major anions, such as SO_4^{2-}, NO_3^- and Cl^- which are expected to influence the acidity of the samples, an ion chromatography system, as described in Section 3.6.5 (page 84), was used for the analyses of these ions. However, due to the limited time of availability of the instrument, not all samples were analysed as the author would have liked. Additionally, other commonly known ions such as NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, and HCO_3^- were not determined. It must be noted that the selected samples were not analysed until a few months after their collection due to the inaccessibility of the instrument at the time. Thus the results presented below should only be regarded as rough estimates, because the concentrations of these anions were expected to be somewhat lower than the actual values due to the lapse of time before analyses.

As March 1983 was the month which had the highest number of acidic samples (9 out of 13 samples), the results for this month were of particular interest to this study, and hence they are presented and discussed below.

5.9.3 Correlations Between the Fluxes of H^+, SO_4^{2-}, NO_3^-, F^- and Cl^-

Although pH or H^+ concentration is commonly used as the main indicator of the severity of the acidic rain problem, the deposition of H^+ is a more accurate measure of the impact on aquatic and terrestrial ecosystems (Whelpdale and Barrie, 1981). Thus, the deposition rates or fluxes of the ions rather than the concentrations (ppm) are used for the following discussion.

Table 5.31 presents the pH, the fluxes of H^+ (as derived from measured pH), excess SO_4^{2-}, NO_3^-, F^- and Cl^- in $\mu g\ m^{-2}\ day^{-1}$, as well as conductivity (a measure for the total amount of soluble inorganic ions), in $\mu s\ cm^{-1}$, and the fluxes of rain ($ml\ m^{-2}\ day^{-1}$) for all available

samples in March 1983. The fluxes were calculated by multiplying the concentrations of each ion ($\mu g\ ml^{-1}$) by the volume of the filtrate of the samples (ml), and then dividing by the number of days of collection and the cross sectional area of the funnel (m^2) on which the precipitation deposited. The analyses of the various ions are given in Section 3.6 (page 79-84).

Table 5.31. Deposition of hydrogen ions and various anions ($\mu g\ m^{-2}\ day^{-1}$) in the lower Tamar Valley, March 1983.

Location	pH	H^+	SO_4^{2-}	Cl^-	NO_3^-	F^-	Con.*	Rain (ml)
1	-	-	-	-	-	-	4.45	-
2	-	-	2663	3239	368	172	8.12	2454
3	4.9	25	2053	2294	443	181	7.30	2013
4	4.4	95	9034	-	-	311	14.64	2390
5	4.3	124	8903	-	322	967	16.68	2480
5B	4.2	140	12559	2626	-	1335	-	2225
6	4.3	106	6267	2674	276	255	13.01	2122
7	-	-	-	-	-	-	-	-
8	5.3	10	1904	3089	59	475	8.12	1980
8B	5.5	6	-	-	-	915	-	1795
9	-	-	3996	3015	272	3036	11.79	2094
9B	5.5	7	-	-	-	2933	-	2365
10	5.7	5	1622	3167	-	207	5.67	2295
11	6.1	2	3338	4630	51	206	10.97	2572
12	5.3	12	2261	7179	429	95	13.42	2385
12B	5.4	9	-	6517	216	-	-	2165
13	5.8	3	2372	3820	276	127	12.60	2122
14	5.2	-	-	-	-	-	4.45	-
15	6.1	2	1406	3384	42	146	6.90	2089
16	5.3	11	2106	-	-	147	5.67	2106
17	6.4	1	11366	7457	79	4769	32.98	2635
17B	4.7	-	-	-	-	-	-	-
17C	4.7	42	-	-	-	3081	-	2110
17D	-	-	-	-	-	-	-	-

* Con. = Conductivity in $\mu m\ s^{-1}$

The excess sulphate was determined by subtracting the estimated marine-derived contribution from the total sulphate, as given by the following equation:

$$SO_4^{2-}\ (\text{excess}) = \text{total } SO_4^{2-} - (2.789/19.90) \times Cl^-,$$

where the factor 2.789/19.90 (or 0.1401) is the sulphate/chloride ratio of the sea-water (Millero, 1974).

The approach for correction of marine-derived contribution to the deposition composition has been found to be a valid one, especially for samples collected in a marine environment (Madsen, 1984). The concentration of sodium is usually used to estimate this contribution, but in this study the concentration of chloride was used instead, as sodium (as Na_3AlF_6 and NaF) was one of the major elements involved in the aluminium smelting process, hence it would not give an accurate estimate of the sea salt contribution. Seven years data from Cape Grim, the baseline air pollution monitoring station in north-west Tasmania, show that there was no significant deviation of Na to Cl ratio in the rainwater samples collected in the marine environment (Ivey, 1986). Thus, if any excess chloride is shown to exist in the lower Tamar Valley, then the excess sulphate calculated for each sample in this study would represent a lower limit.

The Pearson correlation coefficients between the fluxes of any two ions or variables were first calculated for all available samples (Table 5.32), and then for samples only with pH < 5.6 (Table 5.33).

Table 5.32. Pearson correlations between the fluxes of any two ions or variables for all samples collected in March 1983.

	SO_4^{2-}	NO_3^-	Cl^-	F^-	Con.	Rain
H^+	0.6957 (14) P=0.003	0.4869 (10) P=0.122	-0.4564 (11) P=0.078	-0.0359 (16) P=0.448	0.1316 (12) P=0.342	0.0971 (17) P=0.355
SO_4^{2-}		-0.1188 (11) P=0.364	0.7407 (13) P=0.002	0.4774 (15) P=0.036	0.8513 (14) P=0.000	0.2761 (16) P=0.150
NO_3^-			-0.2761 (10) P=0.225	-0.3579 (10) P=0.155	-0.2597 (10) P=0.234	-0.5589 (11) P=0.037
Cl^{-3}				0.1152 (12) P=0.361	0.9946 (11) P=0.000	0.0246 (13) P=0.468
F^-					0.1351 (14) P=0.321	0.5691 (16) P=0.007
Con.						0.0035 (14) P=0.495

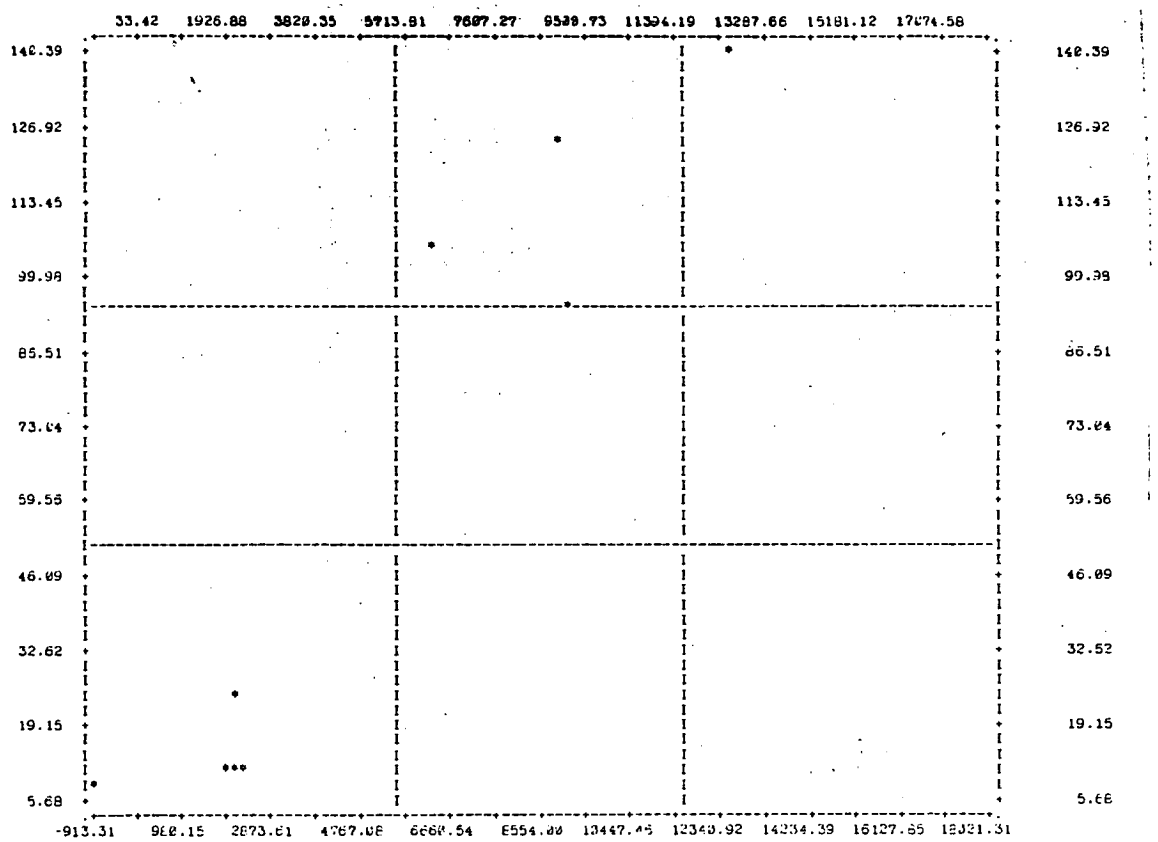
Table 5.33. Pearson correlations between the fluxes of any two ions or variables for acidic samples (pH < 5.6) collected in March 1983.

	SO_4^{2-}	NO_3^-	Cl^-	F^-	Con.	Rain
H^+	0.9430 (9) P=0.000	0.1588 (6) P=0.382	-0.5926 (6) P=0.108	-0.0325 (11) P=0.462	0.8253 (7) P=0.011	0.3365 (12) P=0.142
SO_4^{2-}		0.1309 (7) P=0.390	0.7563 (8) P=0.015	0.6667 (10) P=0.018	0.8993 (9) P=0.000	0.1892 (11) P=0.289
NO_3^-			-0.1324 (6) P=0.401	-0.4966 (6) P=0.158	-0.0808 (6) P=0.440	-0.2865 (7) P=0.267
Cl^{-3}				0.2359 (7) P=0.305	0.9942 (6) P=0.000	-0.0025 (8) P=0.498
F^-					0.5072 (9) P=0.082	0.5033 (13) P=0.040
Con.*						-0.0227 (9) P=0.477

* Con.= Conductivity in $\mu s\ cm^{-1}$.

The hydrogen ions and the excess sulphate were found to be significantly correlated for all samples (r=0.70, p=0.003) (Table 5.32). If only those samples with pH <5.6 were considered, the correlation coefficient was improved greatly (r=0.94, p<0.001) (Table 5.33). This shows the strong linear relationship between the fluxes of H^+ and the excess SO_4^{2-}, as shown in the scattergram (plotted by subprogram SCATTERGRAM of SPSS) between these two variables (Figure 5.15). However, the correlations between hydrogen ions and nitrate, chloride, and fluoride are not significant for all samples or for those with pH <5.6. This implies that SO_4^{2-} is the major acidic species in the acidic samples, and the oil-fired thermal power station is most likely to be the major contributor of this species. Indeed, locations close to the thermal power station, particularly those along the pathway of the SE down-valley flows (i.e. locations 4, 5, and 6) received deposition samples with very low pH (4.2 to 4.4) (Table 5.31). It is possible that other anions such as PO_4^{3-} are also present, but they are assumed to be minor, and hence not considered here.

Figure 5.15. Scattergram for the fluxes of hydrogen versus excess sulphate for acidic samples in the lower Tamar Valley, March 1983. (Correlation coefficient r = 0.94, at significance level p<0.001)



The near absence of correlation between H^+ and F^- (r=-0.03, p=0.46) for the acidic samples indicates that the fluoride ions in the samples might not be derived from hydrogen fluoride, but from other fluoride compounds. However, analyses of more samples in other months are required before any conclusion can be drawn.

It is noted that strong conductivities were associated with the fluxes of excess sulphate and chloride. This is true for all samples (r=0.85 for excess sulphate, 0.99 for chloride, both at p<0.001) and for acidic samples (r=0.90 for excess sulphate, 0.99 for chloride, both at p<0.001). This confirms that sulphate and chloride are two of the major anions in the deposition samples.

Of the various ions, only fluoride appears to correlate significantly with the amount of rain collected, both for all and acidic

samples, while both nitrate and chloride give negative correlations. The correlations of the amount of rain collected with the hydrogen and excess sulphate ions are also insignificant (Tables 5.32 and 5.33). This is to be expected as rainfall is not the only factor which influences the deposition of the various ions in the bulk samples. The kinetic differences in the wet removal processes between various ions, the fog and dew removal processes, the fluxes of dry deposition, and other meteorological conditions such as wind vectors and advection could be as important.

5.9.4 Comparison with Cape Grim Data

Monthly samples of precipitation have been collected at Cape Grim by CSIRO since November 1977, using a 'wet-only' ERNI sampler, which operates only when rain falls and the surface wind is 'baseline' (defined by winds in the 190-280 sector until 4 July 1978 after which an additional criterion of condensation nuclei (CN) counts below 600 cm^{-3} was added; from February 1981 when the CN counters were moved to the new laboratory, until February 1982, wind direction was again the only 'baseline' criterion) (Francey, 1984). These are 'wet-only' deposition samples, and they are routinely analysed for volume, conductance, pH, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, Cl^-, NO_3^-, SO_4^{2-}, alkalinity and insoluble particulates. The monthly data for the period from 1 July 1982 to 1 September 1983 are shown in Table 5.34.

Strictly speaking, these data cannot be compared with those of this study, as they were collected according to different criteria (one for wet deposition, the other for bulk deposition). However, with the knowledge of the neutralization effects caused by the dry deposition of the alkaline species in the bulk deposition samples collected in the lower Tamar Valley (this means the pH of the bulk deposition is higher than the actual wet only deposition), a few comments can still be made if one puts this into perspective.

All monthly samples in Table 5.34 had pH greater than 6.1 except that for the period 1 August 1983 to 1 September 1983, which had a pH of 5.75, the lowest of all samples during the specified period. In other words, no acidic samples (those with pH < 5.6) were collected at Cape Grim. This compares with 31.4% of the total samples measured in the

Table 5.34. Cape Grim monthly rainwater samples, 1 July 1982 - September 1983.

Observational Period	Volume cm^3	Conductivity µS/cm	pH	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}	Alkalinity µe/l
						µm						
1/ 7/82- 2/ 8/82	1375	132.0	6.20	1457.2	25.8	119.3	70.9	0.7	1692.5	6.4	69.2	36.1
2/ 8/82-31/ 8/82	287	140.0	6.32	1213.6	29.2	138.6	43.4	0.7	1650.2	25.0	88.3	7.9
31/ 8/82-30/ 9/82	647	395.0	6.70	2675.1	55.0	327.0	139.7	1.4	2961.9	3.9	104.2	58.7
30/ 9/82- 1/11/82	1347	150.0	6.27	1074.4	39.4	144.0	86.8	5.0	1390.7	12.8	59.9	24.6
1/11/82- 1/12/82	446	490.0	6.68	3297.1	110.0	364.5	132.5	2.1	4259.5	12.1	218.3	57.4
1/ 2/82-31/12/82	92	540.0	6.45	3866.9	66.5	386.7	130.2	2.1	4908.3	10.0	202.7	0.0
31/12/82- 1/ 2/83	640	370.0	6.63	2714.2	76.7	267.4	94.1	0.7	3356.8	1.4	156.0	53.7
1/ 2/83- 3/ 3/83	55	335.0	6.62	2444.5	95.4	257.1	90.6	3.6	3074.8	2.9	244.6	0.0
3/ 3/83-31/ 3/83	490	135.0	6.49	874.3	23.5	105.7	34.7	1.4	1235.5	0.7	59.3	43.7
31/ 3/83-29/ 4/83	1475	365.0	6.51	2179.2	61.1	219.7	74.1	3.6	3244.0	2.1	146.6	27.7
29/ 4/83-31/ 5/83	960	179.0	6.63	1331.0	33.2	153.0	47.4	15.7	1607.9	0.7	82.7	69.6
31/ 5/83-30/ 6/83	1923	140.0	6.11	1083.1	26.6	113.5	38.9	0.7	1348.4	1.4	65.5	24.3
30/ 6/83- 1/ 8/83	705	270.0	6.72	2427.1	47.3	120.1	68.1	12.8	3159.4	16.4	113.2	12.4
1/ 8/83- 1/ 9/83	855	160.0	5.75	1187.5	30.7	137.4	42.4	0.7	1540.2	0.7	63.3	53.2

lower Tamar Valley being acidic during the same period (see Section 5.9.1, page 349).

It is interesting to compare the concentrations of the various ions at Cape Grim and in the lower Tamar Valley for March 1983 (Table 5.35).

Table 5.35. Comparison of acidity and concentration of various anions ($\mu eq.\ l^{-1}$) in the bulk deposition samples in lower Tamar Valley and in the wet deposition samples at Cape Grim for March 1983.

Acidity and composition	Lower Tamar Valley (mean)	Cape Grim
pH	5.2	6.5
SO_4^{2-}	56.2	118.6
Excess SO_4^{2-}	45.7	-170.6
Cl^-	75.5	1235.5
NO_3^-	1.5	0.7
F^-	23.4	-
Conductivity $\mu s\ cm^{-1}$	22.6	135.0
Rain (ml)	2219.9	490.0

In general, the pH of the bulk deposition samples in the lower Tamar Valley for March 1983 were much lower than those of the wet deposition samples at Cape Grim (mean pH of 5.2 was found in the lower Tamar Valley compared with 6.5 at Cape Grim). This means the pH of the actual wet deposition samples in the lower Tamar Valley for this month would be even lower than those at Cape Grim. The higher acidity of the deposition samples in the lower Tamar Valley appears to be caused by the higher concentration of SO_4^{2-} and NO_3^-, and the much lower concentration of Cl^-.

The high conductivity of the Cape Grim sample could be due to the very high concentration of the Cl^-, which are contributed from the marine environment. The volume of precipitation, an important factor which

determines the amount of deposition for the pollution-related species, was about 4.5 times less at Cape Grim compared with the mean volume of precipitation in the lower Tamar Valley.

5.9.5 Analyses of Event Rain Samples

Although monthly bulk deposition samples reflect the chemical constituents and species entering into the atmosphere from various sources, they allow too much time for reactions to occur between precipitation and deposited particulates. This is not very satisfactory for the study of precipitation chemistry. Thus, in recent years, most of the 'acid rain' studies in North America and Europe are restricted to wet deposition, which could be just a particular precipitation event, or a summation of a series of precipitation events (for examples, see Gibson, 1984; Barrie et al., 1984). An event is defined as a single identifiable precipitation occurrence associated with a particular weather pattern (Popp et al., 1984).

As a result of the interesting features of the chemical composition as revealed in the monthly deposition samples, particularly the very high acidity as observed in some of the samples, it was decided to collect some wet deposition or event rain samples for further analyses.

With the assistance of local residents, a total of 24 rain samples was randomly collected from August 1983 to February 1984, using 100 ml specimen containers. The location, date and time of collection are given in Table 5.36. Only pH was measured for the samples (see Section 3.7 on page 84-85).

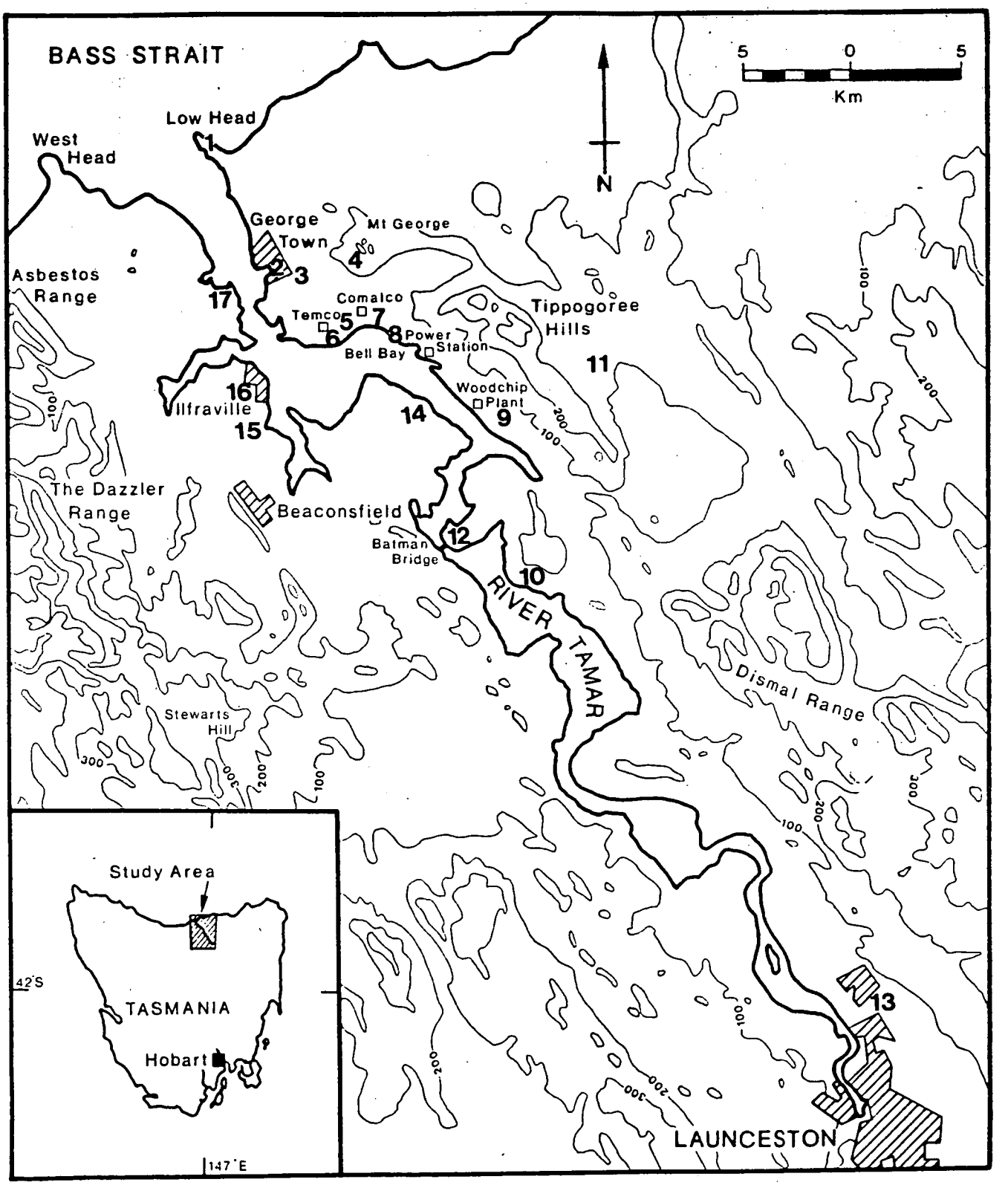
The pH of these rain samples ranged from 4.6 to 7.0. It appears that the acidic rain not only could spread to George Town and Beauty Point, but also travel as far as to Greenhythe and Batman Bridge. The samples collected near Mobil Road (close to the Pioneer cement mixing plant and Temco) in the industrial area had higher pH (6.5 - 6.9), presumably due to more alkaline ions deposited at the location. The rain samples collected overnight at Beauty Point tended to have lower pH than those collected during the day. This could be due to the transport of acidic air pollutants from the industrial area by the NE katabatic winds, which were more frequent in colder months. However, more data are needed before any generalization can be made about this observation.

Table 5.36. pH of wet deposition samples in the lower Tamar Valley.

Location	Date	Hours of Collection	pH
Mobil Road (Bell Bay)	5/8/83	1730 - 1950	6.5
	6/8/83	0830 - 1930	6.9
	16/10/83	2100 - 0730	6.5
Beauty Point	21/7/83	1700 - 0700	5.8
	21/7/83	0800 - 1700	6.1
	31/7/83	1700 - 0800	5.5
	3/9/83	0900 - 1700	5.8
	5/9/83	1730 - 0630	5.7
	-6/9/83		
	7/9/83	1700 - 0700	4.6
	-8/9/83		
	19/9/83	2050 - 0800	7.0
	-20/9/83		
George Town	3/9/83	0830 - 0930	5.4
Rowella (Blackwood Hill)	2/11/83	1300 - 0700	5.6
	8/11/83	1300 - 1800	5.8
Rowella (Clark's Road)	30/11/83	0600 - 1500	6.3
Greenhythe	21/7/83	1500 - 0730	6.0
	31/7/83	0700 - 1430	6.3
	3/9/83	0800 - 1700	6.3
	16/10/83	2100 - 0700	6.1
	17/10/83	0730 - 1330	5.0
	3/11/83	1700 - 2200	6.0
	8/12/83	1300 - 2010	5.9
Soldiers Settlement	30/11/83	0730 - 1200	5.7
	20/2/84	1200 - 2200	5.3
Batman Bridge	8/8/83	2100 - 2130	5.1

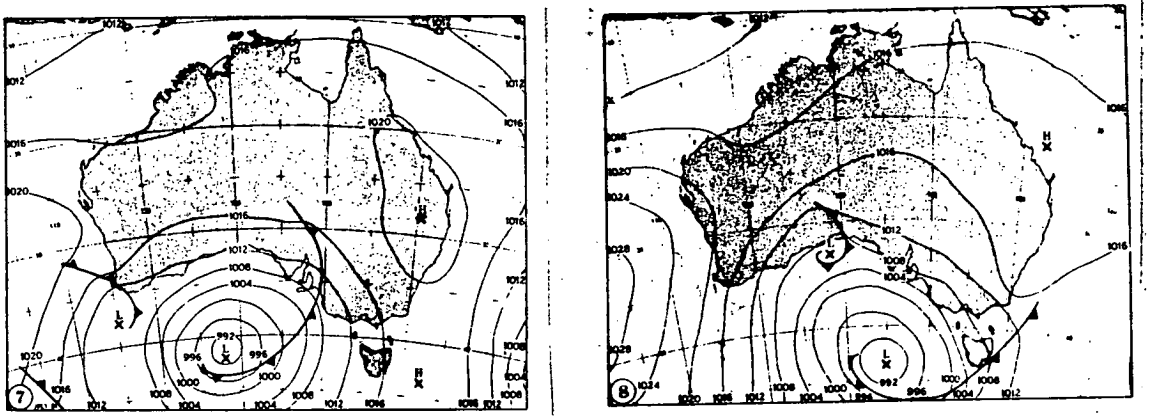
In order to investigate the spatial variation of acidity for a single rain event in the lower Tamar Valley, a total of 17 samples was collected using MS70 Nylex "600" rain gauges (surface area = 35.91 cm^2) from the afternoon of 7th to the morning of 8th July 1984 (see Section 3.7 for further details). The sampling locations are shown in Figure 5.16. With the assistance of local people, the rain gauges were put on the field as soon as the rain arrived, and the samples were collected at the end of the rain event.

Figure 5.16. Sampling locations for an event rain on 7-8 July 1984.



The rainfall was caused by the crossing of a low pressure system from the afternoon of 7th to the morning of 8th (Figure 5.17).

Figure 5.17. MSL synoptic conditions at 0900 hours on 7 July (a) and 8 July (b) 1984 as published by the Bureau of Meteorology.



(a) (b)

The wind direction and speed traces on the recording chart at Station 3 show that NNE to NNW winds were persistent at Station 3 throughout the sample collection period (Figure 5.18).

Figure 5.18. Wind direction and speed traces on recording chart at Station 3 on 7 and 8 July 1984.

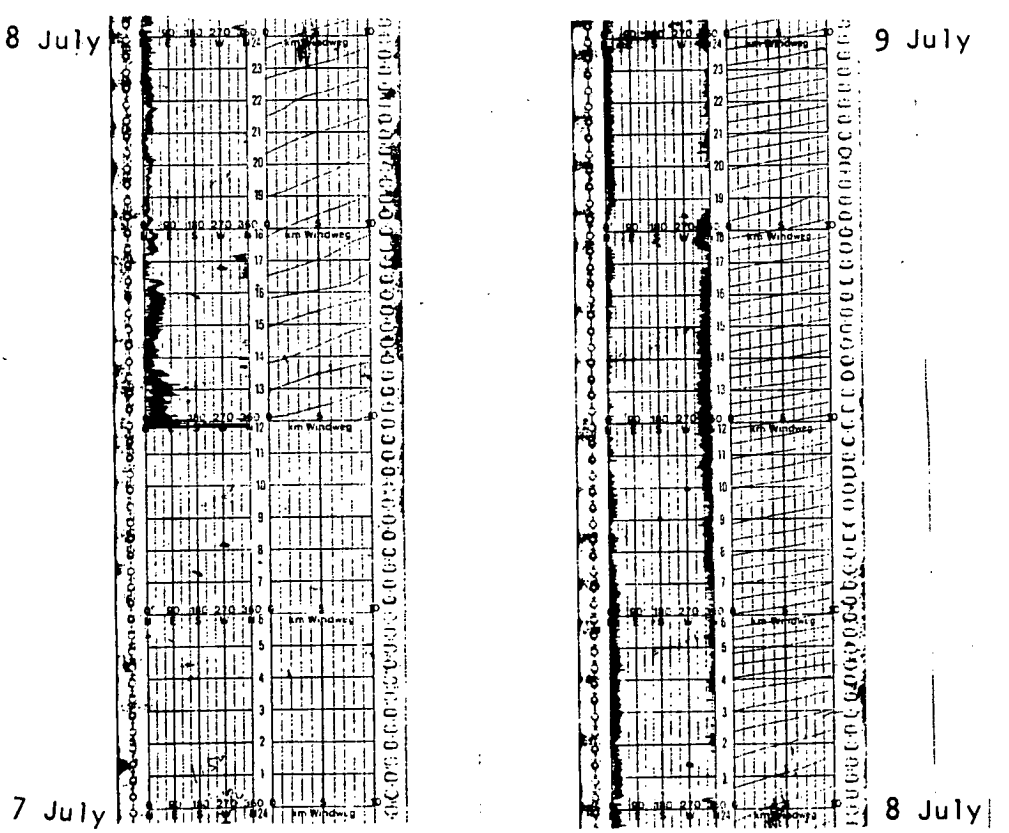


Table 5.37. Chemical composition of event rain (in ppm) on 7-8 July 1984 in the lower Tamar Valley.

Location	Time (Hours)	pH	SO_4^{2-}	SO_4^{2-}(E) (ppm)	NO_3^-	Cl^-	NH_4^+	Rain (ml)
1	1815-0945	5.25	1.22	0.56	0.15	4.68	0.18	26.0
2	1130-1000	5.51	0.61	-	0.07	-	0.18	52.0
3	2000-1100	5.45	0.85	0.45	0.12	2.87	0.18	40.0
4	1305-0940	5.45	0.76	0.48	0.10	1.97	0.10	44.8
5	1242-1005	4.38	1.35	-	0.13	-	0.24	50.4
6	1230-0955	4.86	1.09	-	0.07	-	0.37	42.0
7	1210-1042	5.86	0.87	0.57	0.15	2.12	0.18	54.0
8	1320-1100	5.43	0.81	0.48	0.11	2.33	0.11	56.0
9	1430-1225	5.64	0.67	0.44	0.12	1.63	0.08	84.0
10	2030-0830	5.75	0.39	0.30	0.10	0.64	0.06	22.0
11	1255-0940	5.34	0.53	0.40	0.09	0.94	0.09	92.0
12	1510-1350	4.97	0.61	-	0.07	-	0.11	58.0
13	1930-1615	5.77	0.61	0.33	0.09	2.04	0.13	23.6
14	1540-1315	4.96	0.83	-	0.06	-	0.09	52.0
15	1700-0700	5.22	0.64	-	0.12	-	0.11	-
16	2130-0930	5.16	0.80	-	0.12	-	0.12	-
17	1635-1505	5.23	0.83	-	0.12	-	0.10	48.8

N.B. (1) Locations 5, 7, 9, 11, and 14 were the same as locations 8, 17, 2, 1, and 15 for deposit gauges.

(2) AMC = Australian Maritime College at Newnham (near Launceston).

(3) SO_4^{2-}(E) = Excess sulphate

However, wind shearing effect was evident at low level on the morning of 8th, as the plume from Temco was observed to disperse in the opposite (SE) direction compared with those from Comalco. This shows the complexity of the meteorological factors which influence the dispersion

of emissions from the industrial area during a rain event. Additionally, this illustrates that sometimes it would be misleading to simply use the wind data at Station 3 to generalize the wind field of the whole industrial area. The thermal power station was operating during the sampling period, and fuel oil with 0.5% sulphur (by weight) was used at the time.

The pH and concentrations (in ppm) of the major ions of the samples for this rain event are given in Table 5.37. All anions and the ammonium ions (as nitrogen) were analysed using the ion chromatography system as described before. Fluoride ions were also measured but the concentrations were found at detection limit (0.2 ppm) at most locations except at location 17 (about 1 km ESE of Comalco) and Mt George Motel (3.5 km NW of Comalco), which show a concentration of 0.25 ppm and 0.27 ppm respectively.

The pH of the event rain samples ranged from 4.38 to 5.86. The distribution of the pH of the samples is given in Table 5.38.

Table 5.38. Distribution of pH of the event rain samples, 7-8 July 1984.

Range of pH	No. of Samples
<5.00	4
5.01 - 5.59	9
5.60 - 5.86	4
Total	17

More than three-quarters (13 out of 17) of the samples collected were acidic. Of these, 4 samples had pH < 5.0, and two of these were collected in the industrial area, one at Rowella, and the other near Batman Bridge. The lowest pH measured was 4.38, for a sample collected at location 5, which was in the centre of the industrial area. This shows not only that samples collected in the industrial area could be very acidic, but also that the acidic rain could travel to Rowella and even as far as to Batman Bridge. George Town, Mt George, Low Head, Beauty Point, Ilfraville and Kelso areas all appear to be affected by the acidic rain.

The higher number of acidic samples in the event rain samples tends to suggest that the dry deposition plays a major role in raising the pH of the bulk deposition samples. In other words, the dry deposition is predominantly contributed by the coarser alkaline particles rather than the submicron acidic aerosols. This agrees with the findings of Galloway and Likens (1976), Parkhust et al. (1980), Hansen and Hidy (1982), and Popp et al. (1984).

Table 5.39. Chemical composition of event rain expressed in μeq. l^{-1} on 7-8 July 1984 in the lower Tamar Valley.

Location	Time (Hours)	H^+	SO_4^{2-}	SO_4^{2-}(E)	NO_3^-	Cl^-	NH_4^+	Rain (ml)
				(μeq. l^{-1})				
1	1815-0945	5.62	24.90	11.43	2.42	131.83	12.86	26.0
2	1130-1000	3.09	12.45	-	1.13	-	12.86	52.0
3	2000-1100	3.55	17.35	9.18	1.94	80.85	12.86	40.0
4	1305-0940	3.55	15.51	9.80	1.61	55.49	7.14	44.8
5	1242-1005	41.69	27.55	-	2.10	-	17.14	50.4
6	1230-0955	13.80	22.24	-	1.13	-	26.43	42.0
7	1210-1042	1.38	17.76	11.63	2.42	59.72	12.86	54.0
8	1320-1100	3.72	16.53	9.80	1.77	65.63	7.86	56.0
9	1430-1225	2.29	13.67	8.98	1.94	45.92	5.71	84.0
10	2030-0830	1.78	7.96	6.12	1.61	18.03	4.29	22.0
11	1255-0940	4.57	10.82	8.16	1.45	26.48	6.43	92.0
12	1510-1350	10.70	12.45	-	1.13	-	7.86	58.0
13	1930-1615	1.70	12.45	6.73	1.45	57.46	9.29	23.6
14	1540-1315	10.96	16.94	-	0.97	-	6.43	52.0
15	1700-0700	6.03	13.06	-	1.94	-	7.86	-
16	2130-0930	6.92	15.71	9.39	1.94	62.82	8.57	-
17	1635-1505	5.89	16.94	-	1.94	-	7.14	48.8

N.B. μeq l^{-1} = (ppm/eq. wt) x 1000 , or ((μg/ml)/eq. wt) x 1000

For correlation analyses, it is better to express the concentrations of all ions in μeq. l^{-1} (Table 5.39). The Pearson correlations between the concentrations of various ions (μeq l^{-1}), as well as the volume of rainfall collected during the sampling period for all locations are given in Table 5.40.

Table 5.40. Pearson correlations of the concentrations of various ions (μeq l^{-1}) in 17 event rain samples collected on 7-8 July 1984 in the lower Tamar Valley.

	SO_4^{2-}	SO_4^{2-} (E)	NO_3^-	Cl^-	NH_4^+	Vol
H^+	.6639 (17) P= .002	.3213 (10) P= .183	.0327 (17) P= .450	.4377 (10) P= .103	.4643 (17) P= .030	.0219 (15) P= .469
SO_4^{2-}		.8609 (10) P= .001	.4027 (17) P= .054	.9552 (10) P= .000	.6826 (17) P= .001	-.1881 (15) P= .251
SO_4^{2-} (E)			.8201 (10) P= .002	.6718 (10) P= .017	.6591 (10) P= .019	.1478 (9) P= .352
NO_3^-				.6760 (10) P= .016	-.0102 (17) P= .485	-.0951 (15) P= .368
Cl^-					.7802 (10) P= .004	-.3756 (9) P= .160
NH_4^+						-.2213 (15) P= .214

(COEFFICIENT / (CASES) / SIGNIFICANCE)

The concentration of H^+ was found significantly correlated with the SO_4^{2-} (r=0.66, p=0.002), but not with NO_3^- (r=0.03, p=0.450) and Cl^- (r=0.44, p=0.103). This means that the concentration of H^+ in the samples is bound primarily by SO_4^{2-}, or the high acidity of the samples was predominantly caused by SO_4^{2-} rather than NO_3^- and Cl^-. The low correlations between the concentrations of H^+ and excess SO_4^{2-}, H^+ and Cl^- could be misleading as seven acidic samples, four of which had pH < 5.0, were excluded from the calculations due to missing values. This is confirmed by the fact that the concentration of SO_4^{2-} is correlated very strongly with those of excess SO_4^{2-} (r=0.86, p=0.001) and chloride (r=0.96, p<0.001) ions. The concentration of excess SO_4^{2-} is significantly correlated with those of NO_3^- (r=0.82, p=0.002), chloride (r=0.67, p=0.016) and NH_4^+ (r=0.63, p=0.026), suggesting that these

species may have originated largely from the same source.

The volume of rainfall collected does not seem to correlate significantly with the concentrations of all ions. Except with the concentrations of H^+ and excess SO_4^{2-}, the volume of rainfall gives negative correlation coefficients with other ions.

The correlations between the rates of deposition or fluxes of various ions ($\mu g\ m^{-2}\ hr^{-1}$) were also investigated (Tables 5.41).

Table 5.41. The deposition of various ions ($\mu g\ m^{-2}\ hr^{-1}$) in a rain event on 7-8 July 1984 in the lower Tamar Valley.

Location	Time (Hours)	H^+	SO_4^{2-}	$SO_4^{2-}(E)$ ($\mu g\ m^{-2}\ hr^{-1}$)	NO_3^-	Cl^-	NH_4^+	Rain	R*
1	1815-0945	2.6	552.1	253.4	67.9	2116.9	81.5	452.5	3.7
2	1130-1000	2.0	392.6	-	45.1	-	115.9	643.6	-
3	2000-1100	2.6	631.2	334.2	89.1	2131.3	133.7	742.6	3.8
4	1305-0940	2.0	416.8	263.2	54.8	1405.2	54.8	548.4	4.8
5	1242-1005	27.4	886.2	-	85.3	-	157.6	656.5	-
6	1230-0955	7.5	594.5	-	38.2	-	202.0	546.0	-
7	1210-1042	0.9	580.7	380.5	100.1	1415.0	120.1	667.5	3.8
8	1320-1100	2.7	582.9	345.4	79.2	1676.8	79.2	719.6	4.4
9	1430-1225	2.4	715.0	469.5	128.1	1739.5	85.4	1067.1	3.7
10	2030-0830	0.9	199.1	153.2	51.1	326.7	30.6	510.5	3.0
11	1255-0940	5.6	654.4	493.9	111.1	716.1	111.1	1234.7	4.4
12	1510-1350	7.6	434.6	-	49.9	-	78.4	712.5	-
13	1930-1615	0.5	193.3	104.6	28.5	646.1	41.2	316.7	3.6
14	2130-0930	7.4	557.0	-	40.3	-	60.4	671.0	-
17	1635-1505	3.4	479.9	-	69.4	-	53.1	578.3	-

N.B. (1) $\mu g\ m^{-2}\ hr^{-1}$ = (ppm x Vol. of rain) x 10^4/(35.91 x no. of hours)

(2) Rain expressed in $ml\ m^{-2}\ hr^{-1}$.

(3) R* = Ratio of excess sulphate to nitrate.

The highest deposition of H^+ and SO_4^{2-} occurred at location 5, which was halfway between Comalco and Temco, while the lowest deposition of these two ions occurred at location 13, which was in the campus of the Australian Maritime College at Newnham (near Launceston). On the other hand, the highest deposition of NO_3^- occurred at location 9, which was about 8 km, 7 km and 4 km SE of Temco, Comalco, and the thermal power station respectively, and the lowest at location 13 again. Higher deposition of SO_4^{2-} and NO_3^- were found at locations closer to the industrial sources, with the exception of location 11, which was about 11 km, 10 km ESE of Temco and Comalco, 7 km E of the thermal power station. It is highly likely that the air emissions from the industrial sources, particularly the thermal power station, could be transported over the other side of the Tippogoree Hills. This confirms the findings in Section 5.9.1 (page 347-350).

The ratios of deposition of excess SO_4^{2-} to NO_3^- vary from 3.0 at location 10 (Hillwood) to 4.8 at location 4 (Mt George Lookout), the sampling location with the highest elevation (200 m). On average, the deposition of excess SO_4^{2-} is about 4 times higher than NO_3^-.

Table 5.42. Pearson correlations of the fluxes of various ions ($\mu g\ m^{-2}\ hr^{-1}$) in 17 event rain samples collected on 7-8 July 1984 in the lower Tamar Valley.

	SO_4^{2-}	SO_4^{2-}(E)	NO_3^-	Cl^-	NH_4^+	Vol
H^+	.6268 (15) P= .006	.7021 (9) P= .017	.0760 (15) P= .394	.3436 (8) P= .202	.4792 (15) P= .035	.0839 (15) P= .383
SO_4^{2-}		.9184 (9) P= .000	.6649 (15) P= .003	.8033 (8) P= .008	.6424 (15) P= .005	.5564 (15) P= .016
SO_4^{2-}(E)			.9565 (9) P= .000	.5017 (8) P= .103	.7302 (9) P= .013	.9239 (9) P= .000
NO_3^-				.5142 (8) P= .096	.1988 (15) P= .239	.7698 (15) P= .000
Cl^-					.7023 (8) P= .026	.2449 (8) P= .279
NH_4^+						.2072 (15) P= .229

(COEFFICIENT / (CASES) / SIGNIFICANCE)

The fluxes of hydrogen and sulphate ions are significantly correlated (r=0.63, p=0.006). Unlike the concentrations of hydrogen and excess sulphate, the fluxes of these two ions are significantly correlated (r=0.70, p=0.017). This shows that deposition is a better parameter for correlation analysis than concentration. The flux of hydrogen ions is not significantly correlated with other anions.

If the samples with pH > 5.6 are excluded, the correlation coefficients between hydrogen and sulphate (r=0.79, p=0.002), and between hydrogen and excess sulphate (r=0.93, p=0.012) are greatly improved (Table 5.43). Thus, it appears that the acidity of the event rain samples is largely influenced by the presence of sulphate ions, which certainly have a considerable input from the anthropogenic sources, as evidenced by the high values of excess sulphate ions (Table 5.41).

Table 5.43. Pearson correlations of the fluxes of various ions ($\mu g\ m^{-2}\ hr^{-1}$) in an event rain samples collected on 7-8 July 1984 in the lower Tamar Valley, with all samples of pH > 5.6 excluded.

	SO_4^{2-}	$SO_4^{2-}(E)$	NO_3^-	Cl^-	NH_4^+	Vol
H^+	.7865 (11) P= .002	.9270 (5) P= .012	.1589 (11) P= .320	-.9041 (4) P= .048	.4453 (11) P= .085	.0187 (11) P= .478
SO_4^{2-}		.7053 (5) P= .092	.5631 (11) P= .036	-.5972 (4) P= .201	.5292 (11) P= .047	.2426 (11) P= .236
$SO_4^{2-}(E)$			.9214 (5) P= .013	-.9203 (4) P= .040	.4825 (5) P= .205	.9961 (5) P= .000
NO_3^-				-.7905 (4) P= .105	.0358 (11) P= .458	.6598 (11) P= .014
Cl^-					.0165 (4) P= .492	-.8914 (4) P= .054
NH_4^+						.0365 (11) P= .458

(COEFFICIENT / (CASES) / SIGNIFICANCE)

The rate of rainfall ($ml\ m^{-2}\ hr^{-1}$) correlates significantly with the fluxes of excess sulphate and nitrate. This is true for all samples and for samples with pH < 5.6 (Tables 5.42 and 5.43). The correlation coefficients for excess sulphate are better than those for nitrate in

both cases. This could be due to many factors such as the emission rates of SO_2, NO_x (these are transformed to sulphate and nitrate) from various sources, as well as the rates of their removal in the rainfall. Hidy and Countess (1984) found that sulphate enters cloud or precipitation water by scavenging of particles, or by absorption and oxidation of SO_2, while nitrate may be scavenged as particles, produced in cloud water by absorption of HNO_3 vapour, or by the aqueous chemistry of absorbed nitrogen oxides such as NO_2, NO_3 or N_2O_5 (N_xO_y). HNO_3 is less efficiently scavenged by precipitation than H_2SO_4, possibly due to the kinetic differences in sulphur and nitrogen rainfall removal processes (Morgan, 1982). The removal of the submicron sulphate particles through wet deposition is estimated to have a time constant of the order of 10^{-4} s^{-1}, and a 1-hour rainstorm is likely to remove about 30% of the sulphate particles (United Nations, 1979). For soluble particles, rainout (in-cloud scavenging) removal seems to be more efficient than washout (below-cloud scavenging) (Hidy, 1973; Garland, 1978).

As the rain gauges were operated manually, it was possible that some gauges might fail to collect the initial fraction of precipitation during the rain event because some operators might not be quick enough to respond. Hence, the samples collected might not reflect the total acidity of the entire rain event. The influence of the initial fraction of precipitation on pH seems to depend on the locality of the sampling locations, as studies show that the pH of the initial fraction of precipitation could be higher than the subsequent fractions (Larson and Hettick, 1956; Seymour et al., 1978), or lower (Raynor, 1977; Dawson, 1978; Morgan and Liljestrand, 1980). These reflect the complexity of the factors which influence the time development of precipitation chemistry. The composition of the atmospheric aerosol and the gaseous constituents, cloud physical and chemical dynamics, and meteorological conditions creating the precipitation dictate the properties and the initial acidity or alkalinity of the precipitation (Hansen and Hidy, 1982; Tombach and Pettus, 1982).

Some errors may also be related to the transport and conservation conditions of the rainwater samples (Delmas and Gravenhorst, 1983), but the relative acidities of the samples would not be affected as the samples were all treated similarly.

5.9.6 Chemical Speciation by FT-IR

Fourier Transform Infra-red (FT-IR) spectroscopy has been successfully used in air pollution studies in recent years (for example, see Cunningham, et al., 1974; Tuazon et al., 1978; Gendreau et al., 1980; Bogard et al., 1982; Winer, 1985; McClenny et al., 1985). However, so far its application appears to be concentrated on the identification of chemical components in particulate samples and the trace pollutants in ambient atmosphere. As far as the author is aware, no analyses of precipitation samples by this technique have been reported in the literature, at least in Australia.

The advantages of FT-IR over the conventional IR dispersive or grating spectrometers have been discussed by Griffiths (1975), Henry (1979), and Grim, Fateley and Grasselli (1984). In brief, the major aspects are:

(1) substantial gain in energy or light throughput interferometer;

(2) great improvement of speed, sensitivity, signal to noise ratio, stability, and frequency precision (repeatability) in obtaining high quality spectra;

(3) increase of versatility as all modern FT-IR spectrometers are equipped with a general purpose computer data system which can perform mathematical operations (addition, subtraction, multiplication and division) such as ratioing two spectra against each other to remove absorption bands due to background materials, and also the subtraction of two similar spectra to enhance their differences. However, this advantage is slowly eroding, as many dispersive instruments are now also equipped with microcomputers (Grim, Fateley and Grasselli, 1984);

(4) reference standards can be stored in the computer library for ease of identification of unknown species in the samples.

The chemical composition of some selected deposition samples, particularly those with low pH, was analysed using a Digilab FTS-20E Fourier transform infra-red spectrometer newly acquired by the University in mid-1983. The experiment was very much on a trial basis as no literature on similar work was available.

One microlitre of distilled water (which was used as a reference) and the filtered sample solution were placed respectively between two AgCl windows of 15 mm diameter (each with a circular depression of

0.025 mm) positioned for 0.025 mm pathlength. Unlike KBr, NaCl, CsBr and CsI which, as window material, have been found to be highly prone to ion exchange with a number of inorganic compounds, AgCl is inert to reaction with respect to most inorganic compounds (Nyquist and Kagel, 1971). The windows were held in a micro mull cell, which was then placed on a rectangular holder. The absorption spectra of the distilled water and the sample solution were obtained with 100 scans at 4 cm^{-1} resolution over the range of 4 000-400 cm^{-1} (typically in less than 3 minutes).

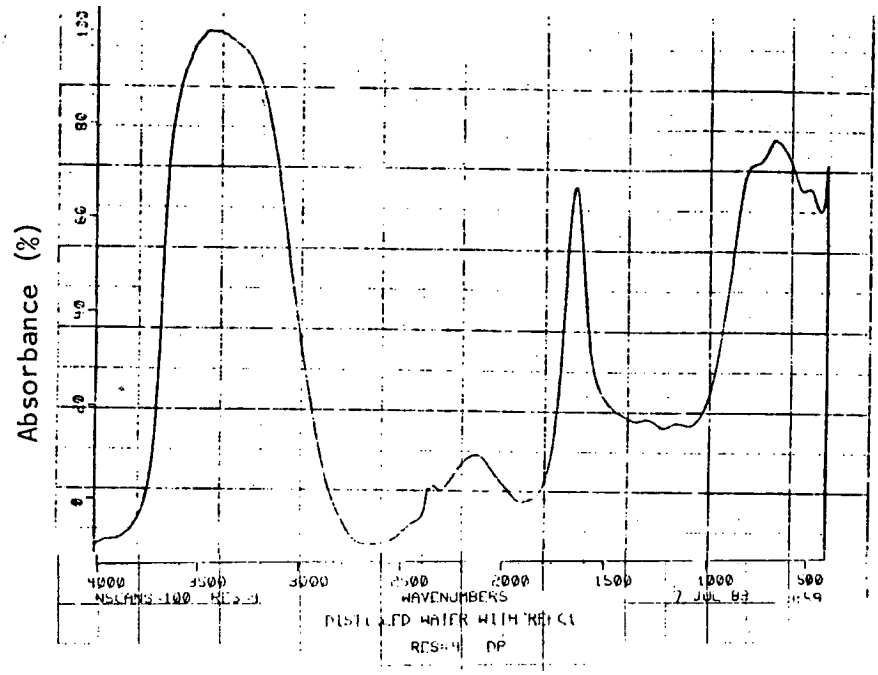
Figure 5.19 shows an example of the spectrum of the distilled water (A), and the result of the computer subtraction of the spectrum of the distilled water from that of a filtered bulk deposition sample of pH 4.8 collected in June 1983 at location 4, about 1 km NW of the Bell Bay thermal power station and 4 km SE of the industrial area. The resulting spectrum (B), apart from displaying the absorption bands due to water (1 620, 3 400, 3 688 cm^{-1}), highlights two of the major acid-producing species, namely SO_4^{2-} (670, 940, 1 170 cm^{-1}) and NO_3^- (832, 1 300, 2 460 cm^{-1}). Sulphate has been found to be the only significant form of sulphur in the fossil fuel particulate emission samples and is essentially the only anion present in water soluble phase (Henry, 1979). Other chemical species found include NH_4^+ (1 400, 1 720, 3 020, 3 280 cm^{-1}), hydrocarbon (2 860, 2 920, 2 970 cm^{-1}), and possibly CN^- (2 125 cm^{-1}).

Figure 5.20 shows the resulting absorption spectrum of a wet-only deposition sample of pH 5.8 collected at Beauty Point from 1700 to 0700 hours on 21 July 1983. The major features in the spectrum, such as the peaks for SO_4^{2-}, NO_3^-, NH_4^+, and possibly CN^- are very similar to those shown in Figure 5.19(B). This suggests that the sources of these chemical species in these two samples could be similar.

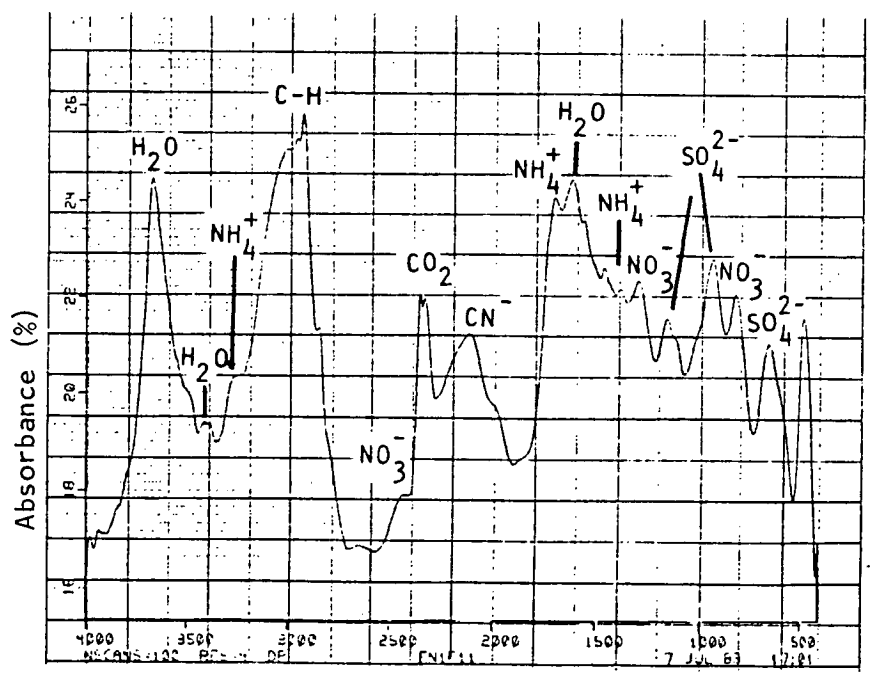
The identification of the chemical species in the sample was achieved through comparison of the absorption spectra of the sample with those of standards or in the literature. Figure 5.21 shows the typical spectra of sulphuric and nitric acids obtained under similar conditions as the precipitation samples except that two microlitres of acids were used for each analysis. The spectra were not smoothed, and the background spectrum due to water was not subtracted from the respective spectrum. Both sulphate (1180 cm^{-1}) and nitrate (1 350 cm^{-1}) ions are

easily identified. It is possible to quantify the concentration of all the chemical species by estimating the infrared band intensities using Beer-Lambert Law.

Figure 5.19. FT-IR absorption spectrum of distilled water (A), and the resulting spectrum of a bulk deposition sample of pH 4.8 with background spectrum due to water subtracted (B)



(A)



(B)

Figure 5.20. FT-IR absorption spectrum of a precipitation sample of pH 6.1 collected at Beauty Point in July 1983 with background spectrum due to water subtracted.

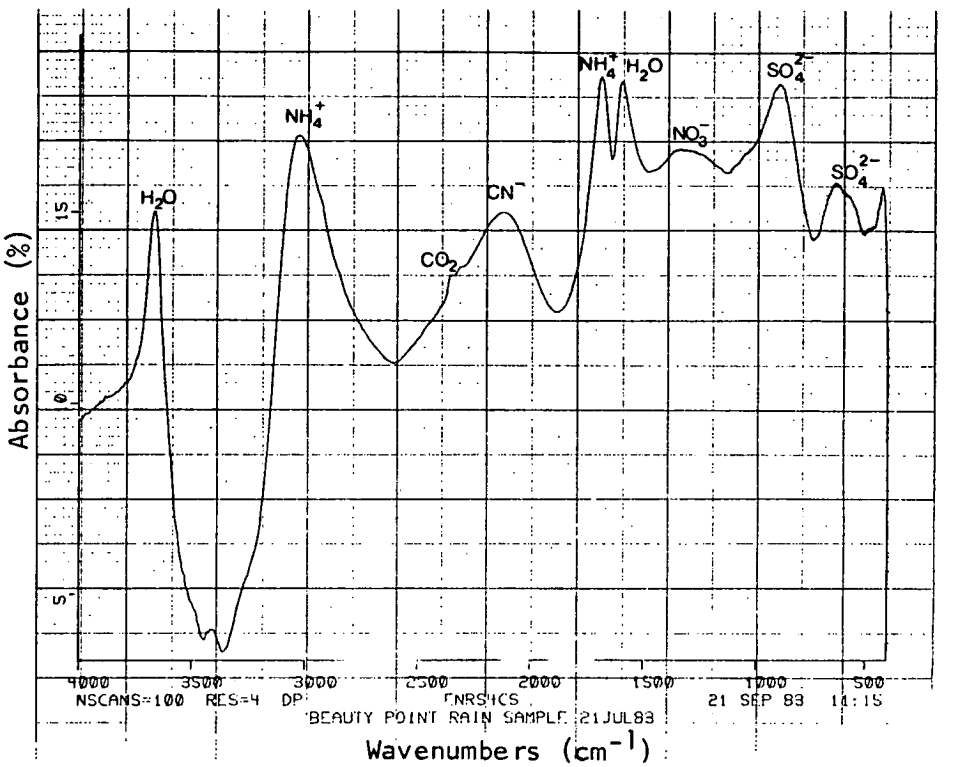
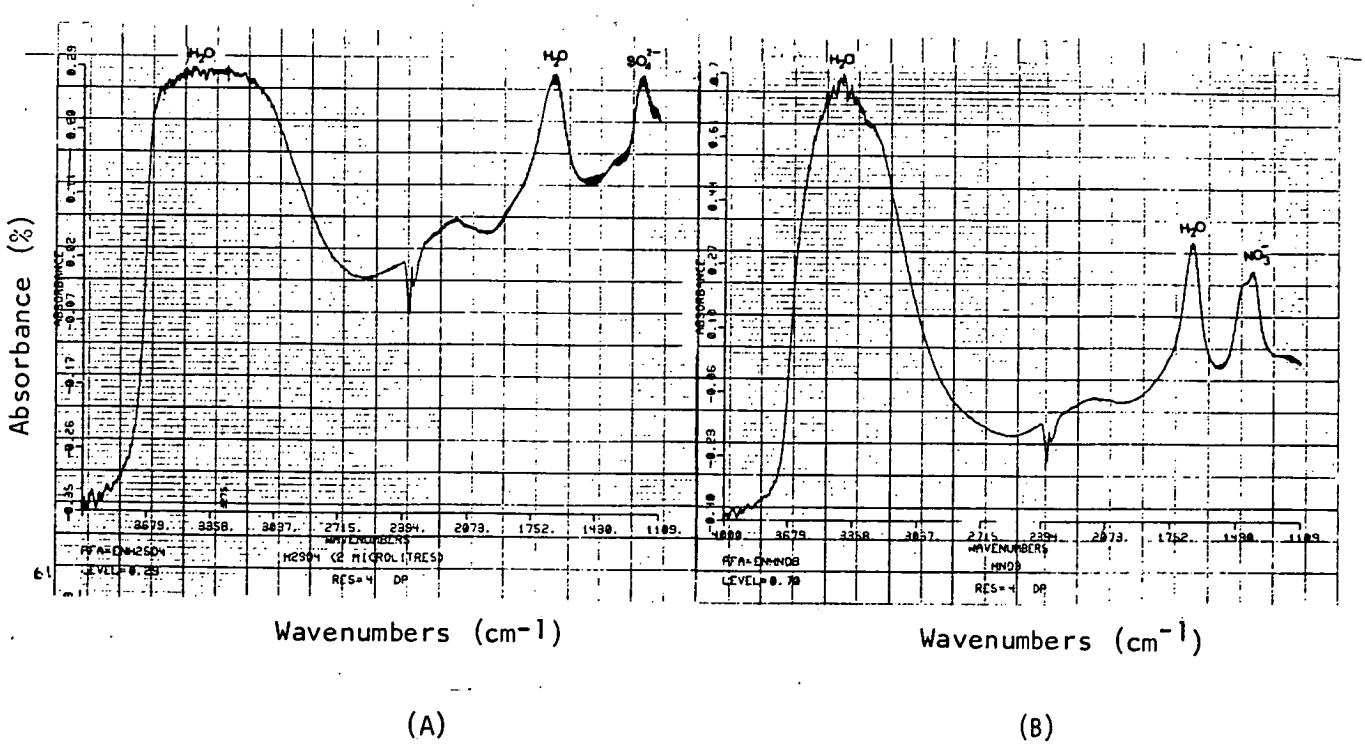


Figure 5.21. FT-IR absorption spectrum of sulphuric (A) and nitric (B) acids. The spectra were not smoothed, and the background spectrum due to water was not subtracted.



The application of FT-IR spectroscopy in analysing precipitation samples proved to be a quick and promising technique especially when a good reference library is available for identification of unknown chemical compounds. In particular, the technique could be used as a complement of other elemental analytical techniques such as SEM/EDAX (for solids) and AAS (for solution).

Unfortunately, the loss of data files twice (once in October 1983 due to the malfunction of the computer system of the instrument, once in June 1984 due to the unintentional mistake of a new operator) has prevented the author from doing further analysis of the stored data.

5.10 Results of High-Volume Air Sampling

Suspended particulates were sampled at various times in 1983 soon after four high-volume samplers were made available from the Department of the Environment, and one from Comalco (see Section 3.9). Although it was the author's intention to run all five samplers at various locations simultaneously as frequently as possible, so as to investigate the spatial variations in the concentrations of the total suspended particulates (TSP) and the metal particulates, the lack of human resources always made this a difficult task.

Most samples were collected using Whatman GF/A glass microfibre filters, while limited samples were collected using Schleicher & Schull membrane filters (0.2 μm porosity). As the membrane filters are very sensitive to moisture, which makes the determination of the mass of TSP difficult, hence they were mainly used for SEM/EDAX analyses.

5.10.1 Concentrations of Total Suspended Particulates and Trace Metals (Al, Mn, Fe and Cu)

Tables 5.44 to 5.52 show the date and time of sampling operations (using glass microfibre filters), as well as the concentrations (expressed as $\mu g\ m^{-3}$) of TSP, Al, Mn, Fe, and Cu at Low Head Pilot Station, Mt George Motel, Mobil Road (near Temco), Temco Road (near Supavinyl Ltd), Bell Bay Port Office, Bell Bay Power Station (near the jetty), Bell Bay Golf Club, Rowella (Blackwood Hills) and Beauty Point respectively. The sampling locations are shown in Figure 5.22.

Table 5.44. High-volume air sampling at Low Head Pilot Station from March to September 1983.

Date of operation	Time	No. of hours	TSP	Al	Mn ($\mu g\ m^{-3}$)	Fe	Cu
19-20 March	1200-1200	24	28.3	0.5	0.8	0.4	<0.1
30 April-1 May	1500-1500	24	26.8	1.4	0.8	0.3	<0.1
18-19 May	2345-1145	12	58.0	1.0	0.3	0.4	<0.1
20-21 May	1345-1345	24	23.2	0.2	0.4	0.2	<0.1
1-2 June	2130-0850	11.3	87.2	8.7	2.1	0.5	<0.1
2-3 June	0900-0900	24	23.4	1.3	0.4	0.2	<0.1
17-18 June	1030-1030	24	56.9	2.0	1.0	0.4	<0.1
1-2 July	2210-0900	10.8	41.5	2.4	0.7	0.1	0.1
2-3 July	1030-1030	24	35.1	1.1	2.5	0.5	<0.1
30-31 August	1730-1900	25.5	38.7	0.2	<0.1	<0.1	<0.1

Table 5.45. High-volume air sampling at Mt George Motel from March to September 1983.

Date of operation	Time	No. of hours	TSP	Al	Mn ($\mu g\ m^{-3}$)	Fe	Cu
19-20 March	1200-1200	24	56.8	0.6	0.9	0.8	0.1
14-15 April	0830-1510	6.7	-	2.2	5.3	2.0	0.1
30 April-1 May	1500-1815	27.3	24.7	0.4	0.2	0.4	0.1
1-2 June	2210-0850	11	120.3	25.8	0.5	0.5	0.2
2-3 June	0905-0905	24	85.3	6.4	0.7	0.6	0.3
1-2 July	2130-2130	24	11.1	<0.1	<0.1	<0.1	<0.1
2-3 July	1010-1010	24	9.1	0.4	0.6	0.2	<0.1
31 July-1 Aug.	2045-0845	12	13.5	<0.1	<0.1	<0.1	<0.1
22-23 August	0700-0700	24	35.4	1.0	1.7	0.6	<0.1
31 Aug-1 Sept	1800-1800	24	30.8	<0.1	<0.1	0.1	<0.1

Table 5.46. High-volume air sampling at Mobil Road, Bell Bay industrial area, from June to December 1983.

Date of operation	Time	No. of hours	TSP	Al	Mn ($\mu g\ m^{-3}$)	Fe	Cu
19-20 March	1500-1500	24	54.5	0.8	0.6	3.9	<0.1
1-2 August	1435-1435	24	56.6	0.5	6.5	4.1	<0.1
30 Sept- 1 Oct	1715-1715	24	12.9	<0.1	4.4	0.7	<0.1
1-2 Oct	1730-1730	24	30.6	0.1	2.8	0.5	<0.1

Table 5.47. High-volume air sampling at Temco Road, Bell Bay industrial area, from September to October 1983.

Date of operation	Time	No. of hours	TSP	Al	Mn	Fe	Cu
					($\mu g\ m^{-3}$)		
26-27 Sept	0930-0930	24	46.8	2.3	0.6	1.0	0.1
26-27 Oct	1045-1045	24	94.7	5.5	0.3	1.5	0.1
29-30 Oct	1730-1730	24	45.0	3.9	0.1	0.4	0.2

Table 5.48. High-volume air sampling at Bell Bay Port Office from June to December 1983.

Dat of operation	Time	No. of hours	TSP	Al	Mn	Fe	Cu
					($\mu g\ m^{-3}$)		
1-2 June	2400-0800	8	21.6	0.8	0.2	0.2	<0.1
2-3 June	0930-0930	24	47.9	3.3	1.2	1.4	<0.1
23-24 June	1600-1600	24	116.5	19.0	2.4	1.0	<0.1
1-2 July	2100-2100	24	4.4	<0.1	0.1	<0.1	<0.1
2-3 July	1000-1000	24	16.3	0.1	0.9	0.5	<0.1
30-31 July	1100-1100	24	33.8	1.0	6.9	1.4	<0.1
1-2 August	1330-1330	24	34.6	<0.1	4.4	1.7	<0.1
28 August	1030-1430	4	91.1	<0.1	23.0	4.3	<0.1
30-31 August	1830-1830	24	97.3	1.0	12.2	3.5	<0.1
31 Aug.-1 Sept	1900-1900	24	117.2	1.0	11.9	5.5	<0.1
1-2 October	1640-1640	24	21.4	<0.1	2.0	0.4	<0.1
14-15 October	1800-1800	24	23.7	0.1	2.4	0.7	<0.1
16-17 October	1700-1700	24	13.6	<0.1	1.7	0.3	<0.1
19-20 December	1800-1800	24	104.5	1.3	6.9	3.5	<0.1
20-21 December	2030-2030	24	98.8	0.9	8.8	4.3	0.1

Table 5.49. High-volume air sampling at Bell Bay thermal power station from October to December 1983.

Date of operation	Time	No. of hours	TSP	Al	Mn	Fe	Cu
					($\mu g\ m^{-3}$)		
1-2 October	1805-1805	24	56.8	0.7	0.6	0.2	<0.1
27-28 October	1125-1325	26	30.4	1.5	0.2	1.5	0.4
29-30 October	1530-1530	24	17.8	0.3	<0.1	0.4	0.5
31 Oct.-1 Nov.	0825-0825	24	11.1	0.1	<0.1	0.1	<0.1
1-2 November	0827-0825	24	38.2	2.0	1.1	0.5	<0.1
4-5 November	1525-1505	23.7	11.1	0.5	<0.1	<0.1	<0.1
5-6 November	1508-1508	24	13.0	<0.1	0.1	0.1	<0.1
6-7 November	1510-1510	24	24.9	0.9	<0.1	0.1	<0.1
7-8 November	1512-2312	32	30.8	1.2	0.4	0.1	<0.1
19-20 November	0830-0930	24	16.1	0.7	0.1	0.3	<0.1
23-24 November	2050-2100	24.2	17.4	<0.1	<0.1	0.2	<0.1
24-26 November	2110-0710	34	14.0	<0.1	<0.1	0.1	<0.1
26-27 Novembe	0712-0735	24.4	18.2	<0.1	<0.1	0.1	<0.1
27-28 November	0737-0713	23.6	16.1	<0.1	<0.1	<0.1	<0.1
28-29 November	0714-0730	24	16.7	<0.1	<0.1	0.1	<0.1
6-7 December	1322-1322	24	20.7	0.5	0.2	0.1	<0.1

Table 5.50. High-volume air sampling at Bell Bay Golf Club from April to October 1983.

Date of operation	Time	No. of hours	TSP	Al	Mn	Fe	Cu
				($\mu g\ m^{-3}$)			
30 April-1 May	1500-1940	28.7	16.5	2.3	<0.1	0.5	0.2
2-3 June	1010-1010	24	16.8	1.0	0.1	0.2	<0.1
3-4 June	1030-1030	24	9.3	<0.1	<0.1	<0.1	<0.1
6-7 August	1005-1005	24	25.2	1.3	<0.1	<0.1	<0.1
31 Aug.-1 Sept	1820-1820	24	58.9	5.9	<0.1	<0.1	<0.1
1-2 September	1825-0940	14.3	25.9	0.6	<0.1	<0.1	<0.1
2-3 September	0945-0945	24	24.6	<0.1	<0.1	<0.1	<0.1
3-4 September	0950-0950	24	36.6	1.4	0.7	0.7	<0.1
4-5 September	1330-1330	24	15.9	0.2	0.1	0.1	<0.1
7-8 September	1010-1010	24	11.5	0.3	<0.1	<0.1	<0.1
28-29 Sept	0845-0845	24	58.3	4.2	<0.1	<0.1	<0.1
29-30 Sept	0845-0845	24	53.0	4.4	0.5	0.5	<0.1
3-4 October	1030-1030	24	11.5	<0.1	<0.1	<0.1	<0.1
4-5 October	1040-1040	24	13.9	<0.1	0.2	0.2	<0.1
5-6 October	1045-1045	24	16.8	0.4	0.2	0.2	<0.1
7-8 October	1025-1025	24	34.2	1.6	2.2	0.8	<0.1
11-12 October	1000-1000	24	11.0	<0.1	<0.1	0.1	<0.1
12-13 October	1025-1025	24	14.0	<0.1	<0.1	0.1	<0.1
13-14 October	1030-1030	24	15.6	<0.1	0.3	0.3	<0.1
17-18 October	1030-1030	24	23.6	1.1	0.3	0.1	<0.1
18-19 October	1035-1035	24	32.4	2.1	<0.1	0.2	<0.1
19-20 October	1035-1035	24	19.0	0.8	0.5	0.1	<0.1
20-21 October	1040-1040	24	24.9	1.0	1.0	0.3	<0.1
25-26 October	0850-0850	24	16.5	<0.1	<0.1	0.1	<0.1
26-27 October	0855-0855	24	20.1	<0.1	<0.1	0.1	<0.1
30 Oct.-1 Nov.	0850-0850	24	12.1	1.2	<0.1	0.1	<0.1

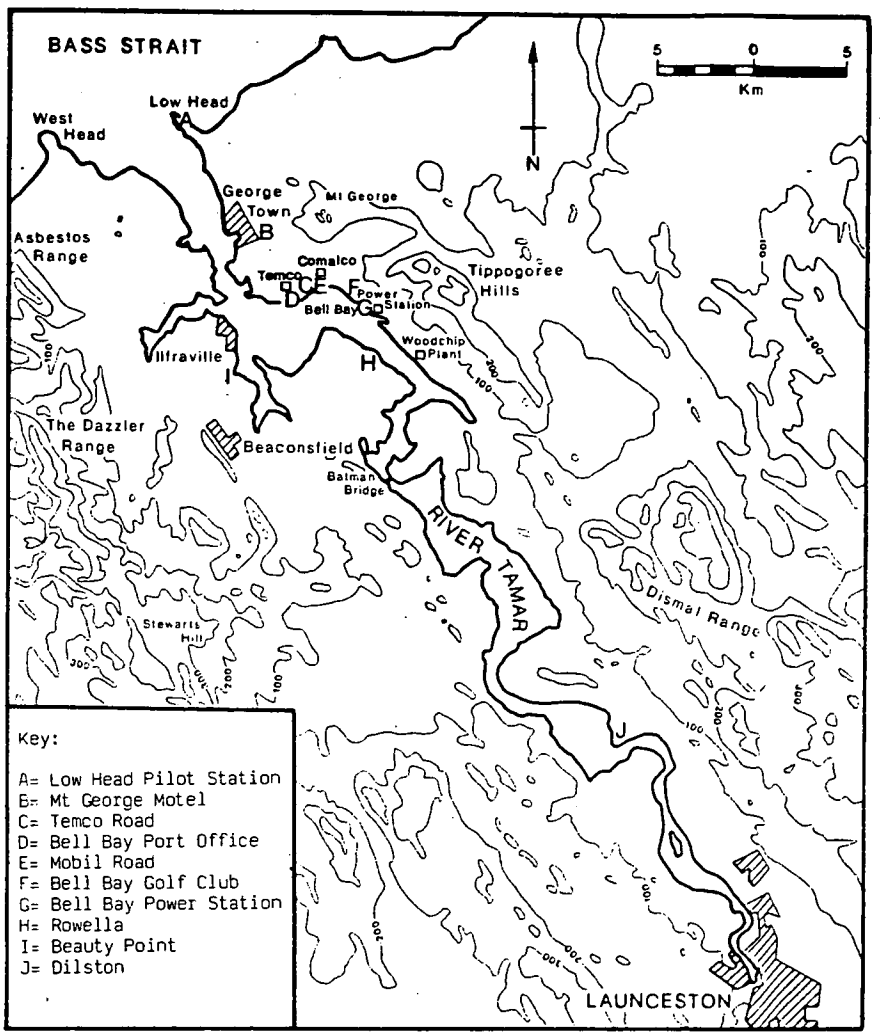
Table 5.51. High-volume air sampling at Rowella from March to August 1983

Date of operation	Time	No. of hours	TSP	Al	Mn	Fe	Cu
				($\mu g\ m^{-3}$)			
19-20 March	1200-1200	24	24.6	0.2	0.1	0.3	<0.1
30 April-1 May	1715-1715	24	10.6	0.3	<0.1	0.2	<0.1
2-3 June	0900-0900	24	14.7	0.6	0.1	0.1	<0.1
26-27 June	0900-0900	24	10.7	0.3	0.2	0.1	<0.1
28-29 July	1635-1635	24	46.2	2.2	0.5	0.2	<0.1

Table 5.52. High-volume air sampling at Beauty Point in August 1983.

Date of operation	Time	No. of hours	TSP	Al	Mn	Fe	Cu
				($\mu g\ m^{-3}$)			
1-2 August	1150-1150	24	10.2	<0.1	<0.1	0.1	0.3
11 August	0940-1325	3.8	26.1	<0.1	0.2	0.1	0.6
16 August	0910-1630	7.3	29.4	0.2	0.2	0.8	0.5

Figure 5.22. Locations where high-volume air samplers were sited.



The siting of the samplers was restricted by the availability of power, as well as of a suitable assistant for some distant locations, such as those on the eastern shore, which the author found inconvenient to service. Thus, more samplings were undertaken on the western shore, particularly at those locations which are expected to be influenced by the NW and SE prevailing winds, and the NE katabatic or channelled winds from the saddle between Mt George and the Tippogoree Hills.

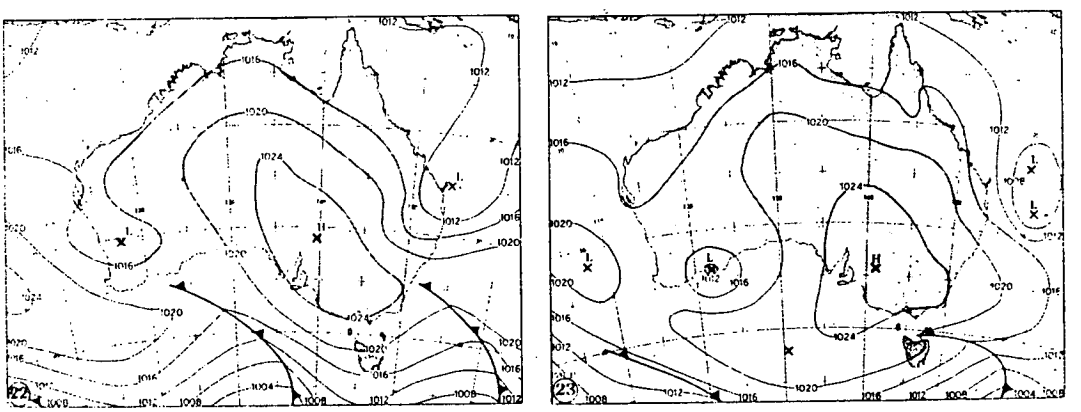
Zn, Ca, and Mg were also measured but their levels in the blank filters were so high and variable that the results were regarded as unreliable, hence they are not included in the tables. Of all trace metals measured, Al and Mn are most useful as they can be used as elemental tracers of air emissions from Comalco (Al) and Temco (Mn).

The 24 hour average concentrations of TSP varied from 23.2 to 56.9 $\mu g\ m^{-3}$ at Low Head Pilot Station, 9.1 to 85.3 $\mu g\ m^{-3}$ at Mt George Motel, 12.9 to 56.6 $\mu g\ m^{-3}$ at Mobil Road, 45.0 to 94.7 $\mu g\ m^{-3}$ at Temco Road, 4.4 to 117.2 $\mu g\ m^{-3}$ at Bell Bay Port Office, 11.1 to 56.8 $\mu g\ m^{-3}$ at the thermal power station, 9.3 to 58.9 $\mu g\ m^{-3}$ at Bell Bay Golf Club, 10.6 to 46.2 $\mu g\ m^{-3}$ at Rowella, and 10.1 to 29.4 $\mu g\ m^{-3}$ at Beauty Point (Australian Maritime College). Measurements were also made for 4 to 14 hours. Some of them showed very high concentrations. It should be noted these ranges are only derived from a limited number of samplings which varied from location to location. They only indicate the concentrations of TSP at a particular location over the stated sampling periods, which were chosen more by convenience than by choice due to the restricted number of field trips the author could make per month, or the availability of the volunteer assistants in the study area. Thus, the number of samplings was biased towards the locations where assistants were more available, and the locations which were more accessible to the author. Of course, the more frequent the sampling is undertaken at a location, the more representative the concentration data. Thus, unless samples were collected simultaneously at all locations, comparisons of the concentrations of TSP and trace metals are not recommended as these could be misleading. The meteorological conditions, particularly the wind vectors, the siting of the high-volume samplers, the particle size distribution, and even the design of the samplers are all expected to influence the concentration of TSP on the filters.

Of all sampling locations, Bell Bay Port Office was the only one which received regular volunteer assistance from the operators in the Port Control room. Thus, the data collected at this location under various meteorological conditions are the best of all. This location is expected to be strongly influenced by the NW and SE prevailing winds, as well as the NE katabatic or channelled (notably easterly) winds coming from the saddle between Mt George and the Tippogoree Hills (see Section 4.5.3, page 168-177). During the limited sampling periods, five out of 15 samples collected at this location had concentrations ranging from 91.1 to 117.2 $\mu g\ m^{-3}$ (one of these was only 4-hr average from 1030 to 1430 hours) (Table 5.48). These values were obtained under different synoptic conditions. For example, the high concentration of TSP

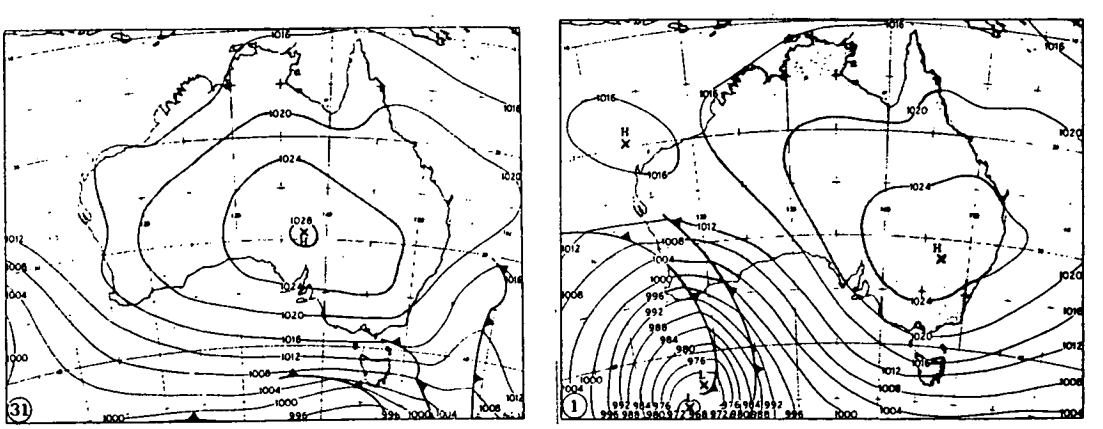
(116.5 μg m^{-3}) on 23-24 June was obtained when Tasmania was under the influence of a slow moving cell of high pressure (Figure 5.23), which resulted in persistent NE katabatic winds from late night to early morning at Station 3. About 16.3% of TSP was contributed by Al, which was about 8 times higher than the concentration of Mn. The higher concentration of Al compared with that of Mn in the sample indicates that Bell Bay Port Office was more affected by the air emissions from Comalco brought by the NE katabatic wind than the air emissions from Temco brought by the NW wind.

Figure 5.23. MSL synoptic conditions at 0900 hours on 22 (a) and 23 (b) June 1983.



(a) (b)

Figure 5.24. MSL synoptic conditions at 0900 hours on 31 August (a) and 1 September (b) 1983.



(a) (b)

On the other hand, the high concentration of TSP (117 μg m^{-3}) on 31 August-1 September was obtained when Tasmania was under the influence of a strong westerly airstream (Figure 5.24), which was channelled into the lower Tamar Valley to become NW wind throughout the day, as evidenced by the wind data at Stations 2 and 3.

The high loading of Mn, which accounts for about 10% of TSP, confirms that the sampling location was more affected by the air emissions from Temco than those from Comalco during the sampling period. Similar observations were made on 28 August when the sampler was run for 4 hours (from 1030-1430 hours) when NW wind was prevailing. On this occasion, the concentration of Mn was as high as 25.2% of TSP.

Higher concentrations of Mn at the Bell Bay Port Office were associated with higher concentrations of Fe (the ratio of Mn to Fe varied from 2.2 to 3.5 during those sampling periods with high Mn concentrations (i.e. > 10 μg m^{-3}). This further suggests that the major source of Mn and Fe is Temco where Fe-Mn alloy, among others, is manufactured. The concentrations of Cu were generally < 0.1 μg m^{-3}.

In general, Bell Bay Port Office appears to be more affected by the air emissions from Temco than those from Comalco, as evidenced by the higher Mn loading in most samples. This is to be expected because of the consistently higher frequency of occurrence of NW wind compared with that of NE wind (see Table 4.17 on page 134).

The upper limits of the 24 hour average concentrations of TSP and Mn measured in the industrial area exceeded 100 μg m^{-3} and 10 μg m^{-3} respectively. These seem to be comparable to or higher than the ambient air standards adopted in some countries (Table 5.53). However, it should be noted that unless similar sampling techniques (preferably with similar filters, or with filters of similar collection efficiencies) are used, the comparison of the concentrations of TSP or Mn between two places may not be applicable. No ambient air standard for TSP, Mn or Al are available in Tasmania. Higher concentrations of TSP generally correspond with higher concentrations of Al or Mn, or both, suggesting the strong emission-receptor relationship.

Apart from Bell Bay Port Office, other locations where high concentrations of TSP had occasionally been measured were Low Head Pilot Station and George Town Motel (Tables 5.44 and 5.45).

Table 5.53. Ambient air standards (24-hour average) for total suspended particulates, Mn in various countries (Source: Newill, 1977)

Country	24 hour average concentration ($\mu g\ m^{-3}$) TSP	Mn
Colombia, Japan	100	-
Canada - Acceptable level	120	-
Bulgaria, Czechoslovakia, East Germany	150	10
Romania, USSR	150	10
Finland, Hungary, Turkey	150	-
Israel	200	10
Poland	75	(non-industrial area)
	200	(industrial area)
Italy, Spain	300	-
United States	260	(Primary)*
	150	(Seconadry)*

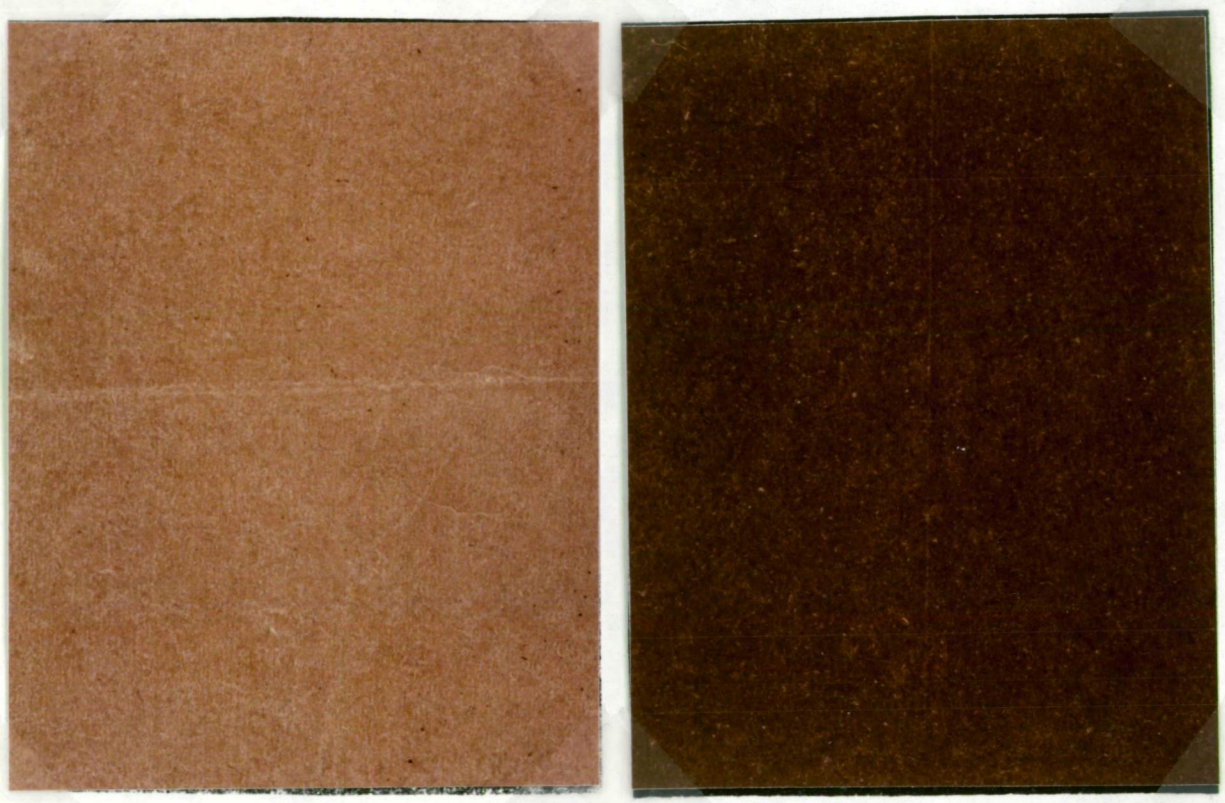
* Maximum concentration not to be exceeded more than once per year.
N.B. WHO (1979) interim guidelines: 150-230 $\mu g\ m^{-3}$ (24 hour values).

Unfortunately, the number of samplings at Mobil Road and Temco Road, both of which are within the industrial area, are too small to be representative. Although the concentrations of TSP at these two locations during the sampling periods were mostly below 60 $\mu g\ m^{-3}$, the loadings of Al (for Temco Road) or Mn (for Mobil Road) were relatively high, varying from 5.0% to 8.7% for Al at Temco Road, and 9.2% to 34.1% for Mn at Mobil Road. In fact, the lowest concentration of TSP collected on 19-20 December at Temco Road (12.9 $\mu g\ m^{-3}$) contained the highest loading of Mn, which accounted for 34.1% of TSP.

The data at Rowella and Beauty Point are also too few to be representative. All concentrations measured at Bell Bay Golf Club and the thermal power station were also below 60 $\mu g\ ^{-3}$. However, there is evidence to suggest that air emissions from Comalco and Temco could reach these two locations, as shown by the high loadings of Al (10% of TSP) on 31 August-1 September at Golf Club, and Mn (5.2% of TSP) on 1-2 November at the power station.

The presence of Mn particulates on the filters can be visually detected, as shown by the characteristic brown colour in Figure 5.25(A). The dark brown colour of the sample shown in Figure 5.25(B) indicates that apart from Mn, the filter has also collected pollutants from other sources.

Figure 5.25. High-volume air samples collected at Mobil Road from 1715 to 1715 hours on 30 September-1 October 1983 (A), and at Bell Bay Port Office from 1800 to 1800 hours on 19-20 December 1983 (B). Glass microfibre filters were used. Manganese accounts for 34.1% and 6.6% of TSP for the respective samples.



(A) (B)

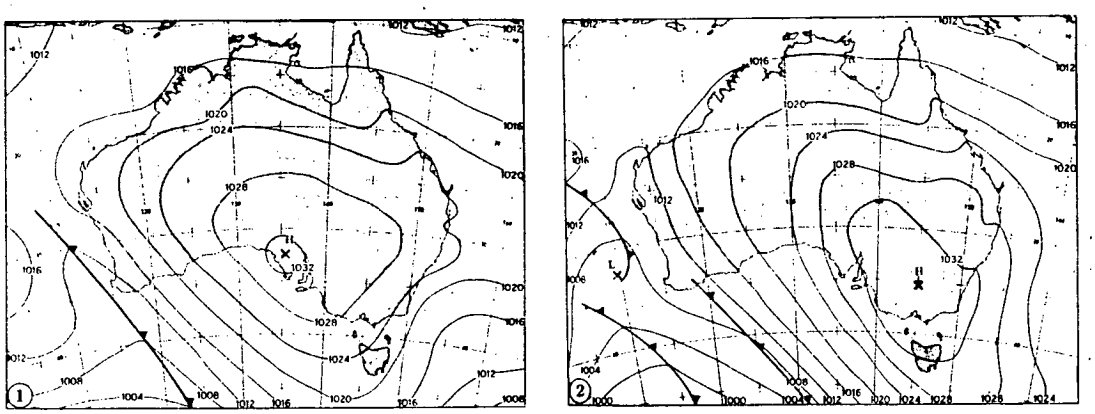
5.10.2 Spatial Variation of Concentrations of TSP and Trace Metals During a Nighttime Inversion

Table 5.54 shows the spatial variation of the concentrations of TSP and major trace metals collected during nighttime (as defined in Chapter 4) on 1-2 June 1983 when Tasmania was under the influence of a large high pressure cell which brought a light W to SW airstream to the State (Figure 5.26). The wind data at Station 2 (Point Effingham) show that SW wind was presistent from 2100 to 2330 hours (with an hourly mean speed of 2.5 m s^{-1}), followed by S to SE down-valley flows which prevailed until noon of 2 June. Wind data from Stations 1 (Low Head) and 3 (1 km ESE of Comalco) are not available due to malfunction of the anemometers at the time. There is evidence to suggest that a low level inversion was prominent from 1700 to 0500 hours on 1-2 June, with a lapse rate of -5.9 ^{o}C/ (see Table 4.54, page 283).

Table 5.54. High-volume air sampling at various locations on 1-2 June 1983.

Location	Time of operation	Hours	TSP	Al	Mn	Fe	Cu
				($\mu g\ m^{-3}$)			
Low Head Pilot Stn.	2130-0850	11.3	87.2	8.7	2.1	0.5	<0.1
Mt George Motel	2210-0850	11	120.3	25.8	0.5	0.5	0.2
Bell Bay Port Office	2400-0800	8	21.6	0.8	0.2	0.2	<0.1

Figure 5.26. MSL synoptic conditions at 0900 hours on 1 (a) and 2 (b) June 1983.



(a) (b)

It was most interesting to observe the dispersion of air emissions from the industrial area during this inversion night in early winter, the meteorological conditions of which could be fairly typical. When the author visited the industrial area at about 2230 hours, the area was completely covered by smog (fog mixed with air emissions from the two metal smelting industries) which resulted in very poor visibility (< 100 m). However, the Tamar River close to the industrial area was very clear at the time, possibly due to the influence of the SW wind which kept the smog away from the river. About an hour later, the smog had extended to the river, which was then no longer visible. Presumably the smog was either advected to the river due to warmer water temperature, or transported by the NE katabatic wind which is expected to be persistent for brief periods (this could not be confirmed with the loss of wind data at Station 3). It is reasonable to deduce that S to SE winds were also prevailing at Station 3 during most hours in the morning of 2 June like those observed at Station 2.

Both Low Head Pilot Station and Mt George Motel collected very high concentrations of TSP. The high loadings of Al at these two locations, which accounted for about 10% and 22% of TSP respectively, suggested that the sampling locations were strongly influenced by the air emissions from the aluminium smelter, most likely brought by the S to SE down-valley flows. Low Head Pilot Station had the highest concentration of Mn even though it is furthest from Temco. This could be due to the fact that it is more in the pathway of the SE down-valley flows with respect to Temco compared with the other two locations.

The low concentrations of TSP and trace metals at Bell Bay Port Office indicated that the sampling location was not exposed to the air emissions as much as the others because of the SW and S to SE winds which were prominent during most of the sampling period. Strictly speaking, these concentrations cannot be compared with those at the other two locations because of the different sampling periods (Table 5.54).

5.10.3 Spatial Variations of Concentrations of TSP and Trace Metals When SE and NW Winds Were Persistent

Table 5.55 summarises the data for Low Head Pilot Station, Mt George Motel, and Bell Bay Port Office when SE ambient wind was persistent throughout the day in the lower Tamar Valley on 2-3 July 1983.

Table 5.55. High-volume air sampling at various locations on 2-3 July 1983. All samplers were run for 24 hours.

Location	Time of operation	TSP	Al	Mn	Fe	Cu
				($\mu g\ m^{-3}$)		
Low Head Pilot Stn.	1030-1030	35.1	1.1	2.5	0.5	<0.1
Mt George Motel	1010-1010	9.1	0.4	0.6	0.2	<0.1
Bell Bay Port Office	1000-1000	16.3	0.1	0.9	0.5	<0.1

Low Head Pilot Station had the highest concentrations of TSP, Al and Mn, though it is furthest from the industrial area. Thus, the concentration of TSP is not necessarily decreasing with the distance from the emission source. The particle size distribution and the wind conditions greatly influence the dispersion of the air pollutants.

Table 5.57. High-volume air sampling at various locations on 31 August-1 September 1983. All samplers were run for about 24 hours.

Location	Time of operation	Hours	TSP	Al	Mn	Fe	Cu
				($\mu g\ m^{-3}$)			
Low Head Pilot Stn.	1730-1900	25.5	38.7	0.2	<0.1	<0.1	<0.1
Mt George Motel	1800-1800	24	30.8	<0.1	<0.1	0.1	<0.1
Bell Bay Port Office	1830-1830	24	117.2	1.0	11.9	5.5	<0.1
Bell Bay Golf Club	1820-1820	24	58.9	5.9	<0.1	<0.1	<0.1

In contrast to the persistent SE ambient wind on 2-3 July, NW ambient wind was persistent throughout the sampling period on 31 August-1 September 1983. Bell Port Port Office, being closest to Temco (about 1 km SE of the alloys plant), collected the highest concentrations of TSP (Table 5.57). The high loading of Mn (10.2% of TSP) in the sample suggested that it was strongly influenced by the air emissions from Temco. Bell Bay Golf Club, about 2.5 km SE of Comalco, seemed to be more influenced by the air emissions from Comalco, as evidenced by the high loading of Al (10% of TSP) in the sample. Relatively low concentrations of TSP and trace metals at Low Head Pilot Station and Mt George Motel were measured because these locations were upwind of the emission sources during the sampling periods; but the concentration of TSP at Low Head Pilot Station was about 20% higher, possibly caused by the sea-spray as the sampling location was nearest to the coast.

5.10.4 Correlation of Wind Speeds with Concentrations of TSP

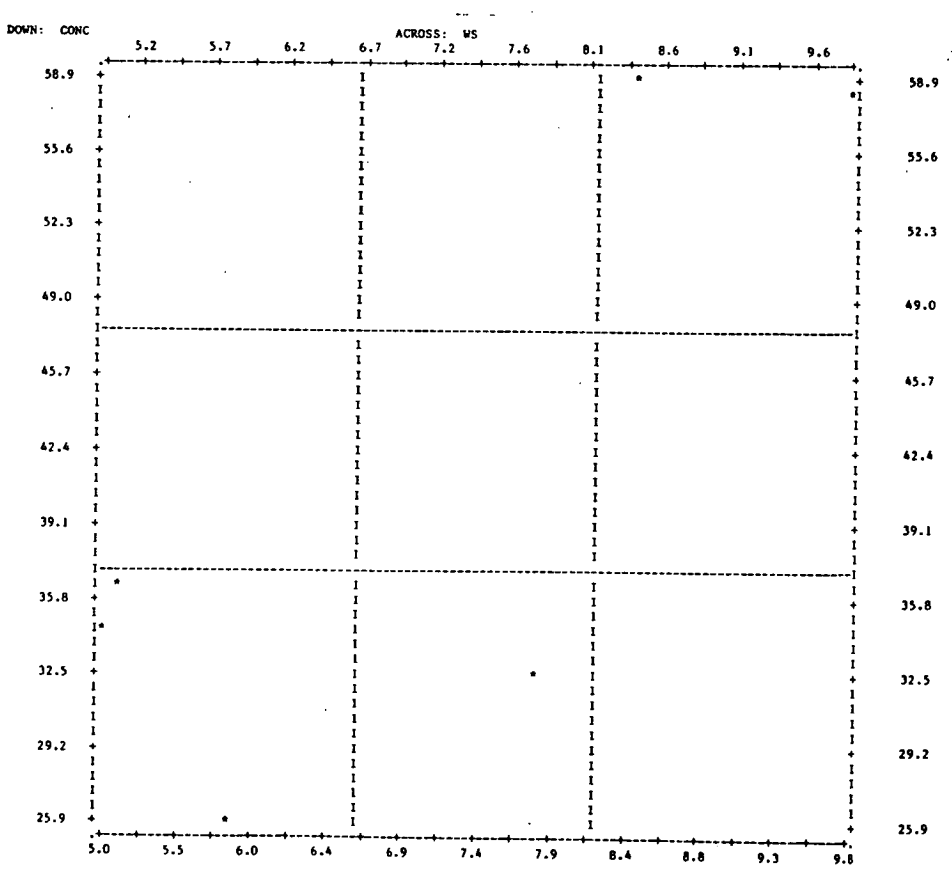
In order to correlate the strength of wind speeds with the concentrations of TSP, sampling locations which were downwind (NW or SE) of the industrial area are investigated. Only winds (NW or SE) which were persistent throughout the sampling periods are considered. This makes the sampling location at Bell Bay Golf Club the best choice because: (1) more persistent NW winds happened to be recorded at this location than other locations during the various sampling periods; (2) it was only about 1.5 km SE of Station 3. Thus, the wind speed data of this station are conveniently used (with reasonable justification when only the NW wind is considered) for the correlation analysis (Table 5.58).

Table 5.58. Data for wind speed and concentrations of TSP at Bell Bay Golf Club.

Date of operation	Time	No. of hours	TSP ($\mu g\ m^{-3}$)	Wind speed at Station 3 ($m\ s^{-1}$)
31 Aug.-1 Sept	1820-1820	24	58.9	8.4
1-2 September	1825-0940	14.3	25.9	5.8
3-4 September	0950-0950	24	36.6	5.8
28-29 Sept	0845-0845	24	58.5	9.8
7-8 October	1025-1025	24	34.2	5.0
18-19 October	1035-1035	24	32.4	7.8

In general, higher wind speeds tended to result in higher concentrations of TSP. Based on the calculation of Pearson correlation coefficient, it is found that the wind speeds and the concentrations of TSP are significantly correlated, with a correlation coefficient of 0.77 at 3.7% significance level. The scattergram of the concentration of TSP versus the wind speeds is shown in Figure 5.27.

Figure 5.27. Scattergram for the concentrations of TSP versus wind speeds at Bell Bay Golf Club. (Correlation coefficient r=0.77, p=0.037)



5.11 Analyses of Airborne Particulates by SEM/EDAX

Complementary to the elemental analyses performed by using the atomic absorption spectroscopy, scanning electron microscopy (SEM) and energy dispersive analysis of X-ray (EDAX) are also used to characterise the chemical composition of some selected samples of airborne particulates. SEM/EDAX are particularly useful for identifying Si (this remains one of the major air emissions from Temco), S and their compounds, which are not readily analysed by flame AAS because of the tedious preparation required. Moreover, the particle size distribution of the airborne samples, which can be easily differentiated by SEM, is also of interest to this study, though a detailed analysis on this aspect was not planned.

(A) Particle Size Distribution

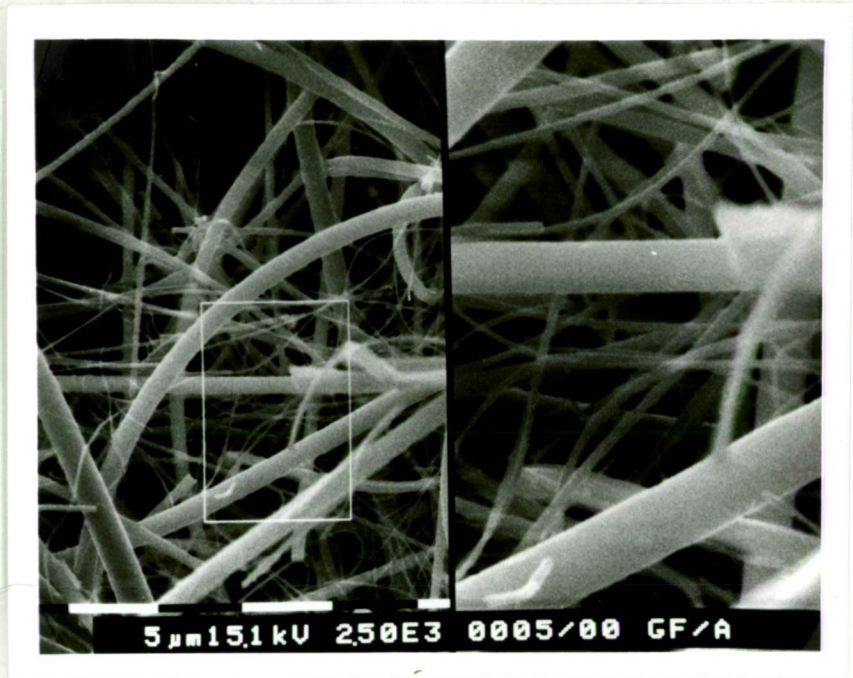
Figures 5.28 and 5.29 show the electron micrographs of a blank Whatman GF/A glass microfibre filter and a blank Schleicher & Schull membrane filter taken by the Philips 505 scanning electron microscope, and Figures 5.30 to 5.35 show the airborne particulates collected by these two types of filters. Most particles collected by either filter were less than 10 μm, though occasionally particles with larger sizes were also collected (Figures 5.33 and 5.35).

(B) EDAX Spectra

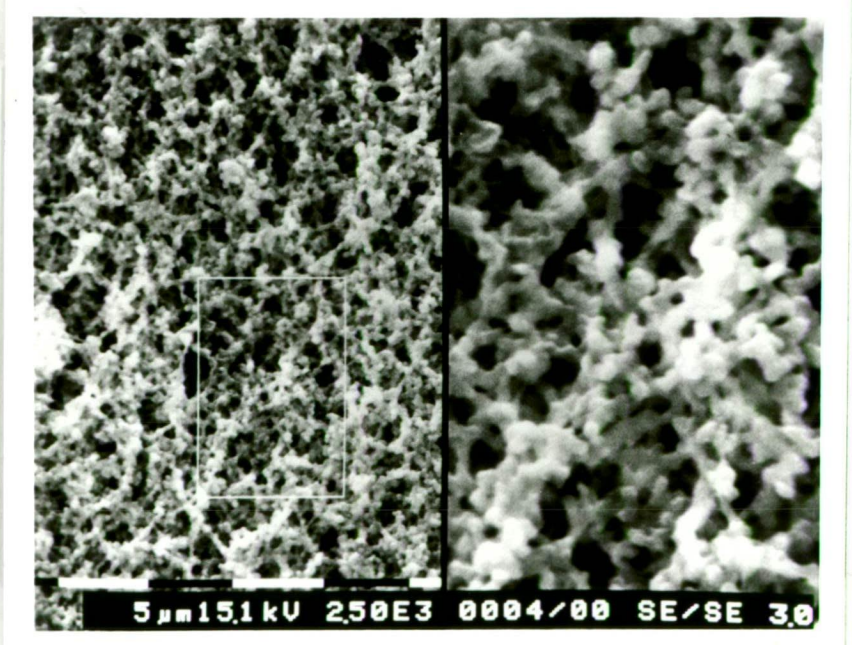
While the Philips 505 scanning electron microscope produces good electron micrographs, no chemical analysis is possible with this instrument. This major drawback is overcome by analysing the similar samples using the electron probe microanalyser (see Section 3.9.2 in Chapter 3) which allows the identification of various chemical elements from their characteristic X-ray spectra.

The glass microfibre filter, as a medium for deposited particulates, is not very suitable for electron probe microanalysis because airborne particles could be embeded within the fibres of the filter. This makes qualitative and semi-quantitative assessment of the composition of the particles difficult in view of the high levels of background impurities, which might interfere in the analyses.

Figure 5.28. Electron micrographs of a blank Whatman GF/A glass microfibre filter (A) and Schleicher & Schull membrane filter (B) (magnification: 2500X (left) and 7500X (right).



(A)



(B)

Figure 5.29. Electron micrograph (magnification 2500X) showing airborne particles (< 5 µm) collected by a glass microfibre filter.

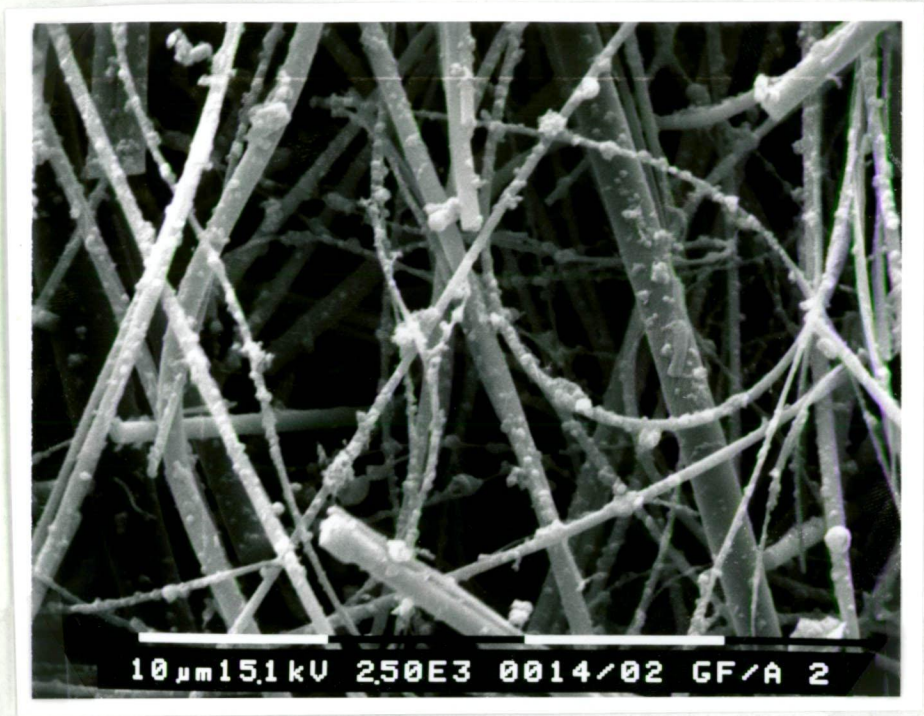


Figure 5.30. Electron Micrograph (magnification 1490X) showing a large particle (30 x 50 µm) deposited on the glass microfibre filter.

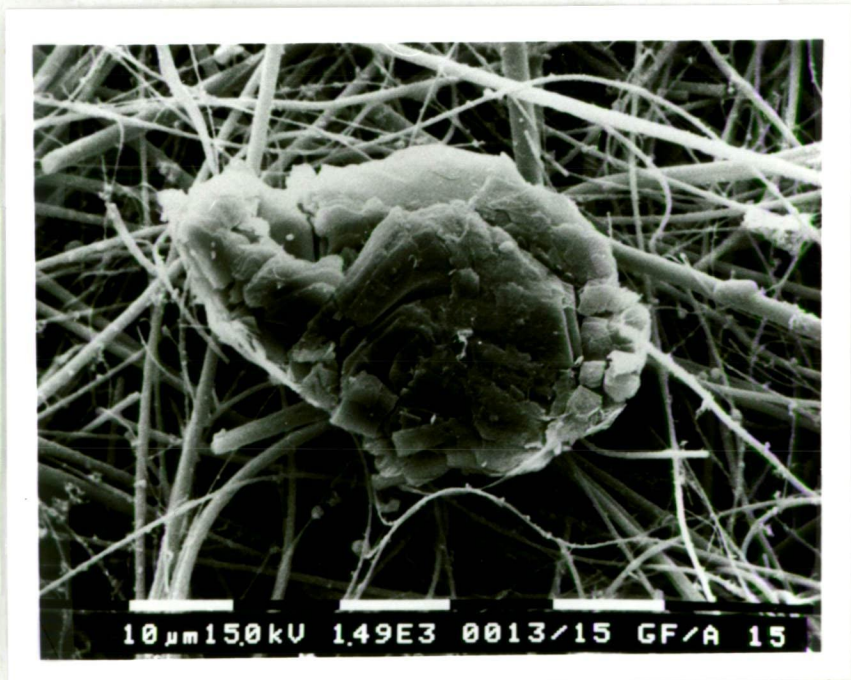


Figure 5.31. Electron micrograph (magnification 1010X) showing airborne particles (< 10 μm) collected by a Schleicher and Schull membrane filter. This particular sample was collected at Bell Bay Port Office. X-ray microanalysis shows that this sample contained predominantly Mn.

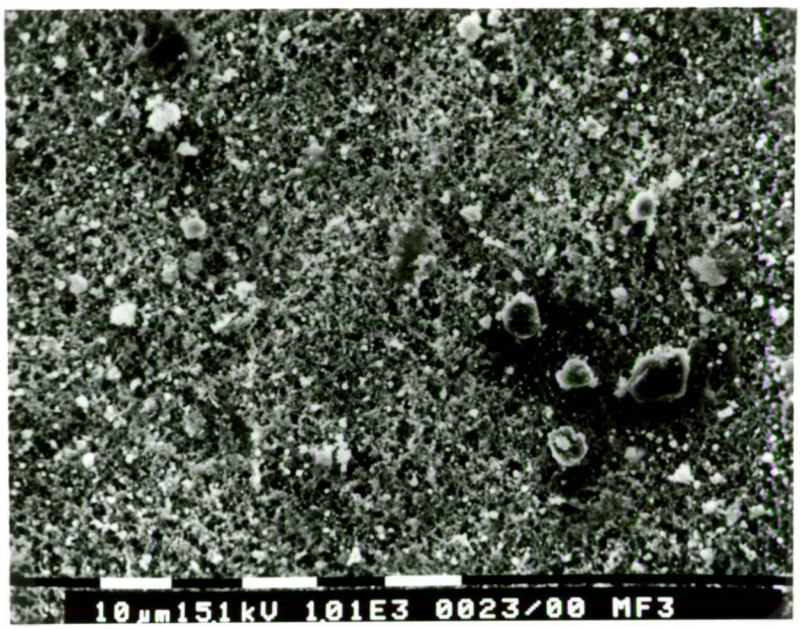


Figure 5.32. Electron micrograph (magnification 252X) showing airborne particles with various sizes deposited on a membrane filter. This sample was collected at Dilston. X-ray microanalysis shows that it mainly contained Al, Fe, Si, S and Cl. The dark shadows around some larger particles were caused by the charging effect. This shows the fragility of the membrane filter compared with glass microfibre filter.

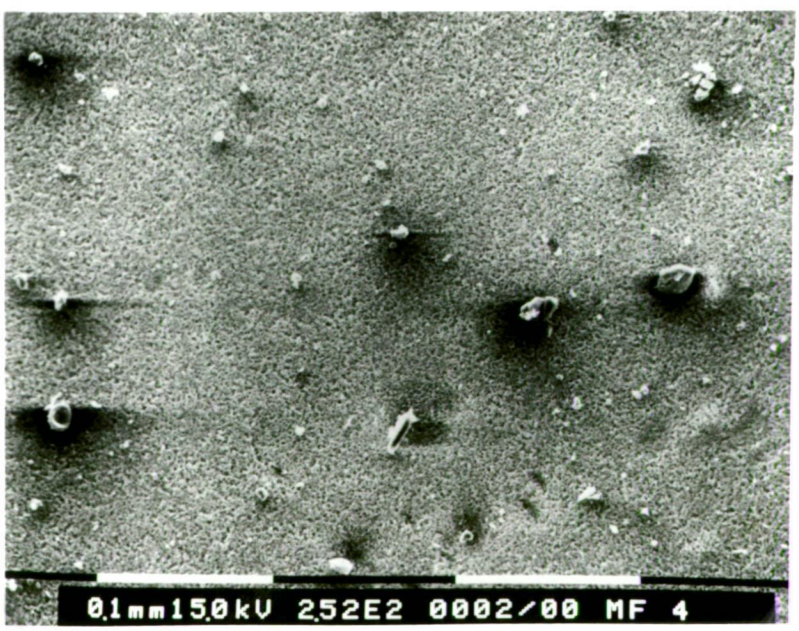
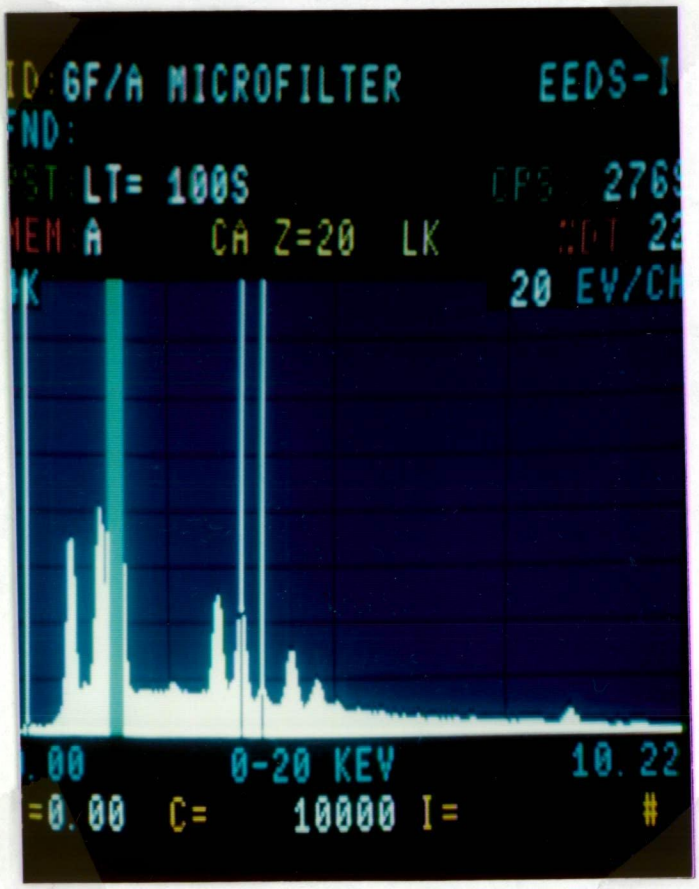


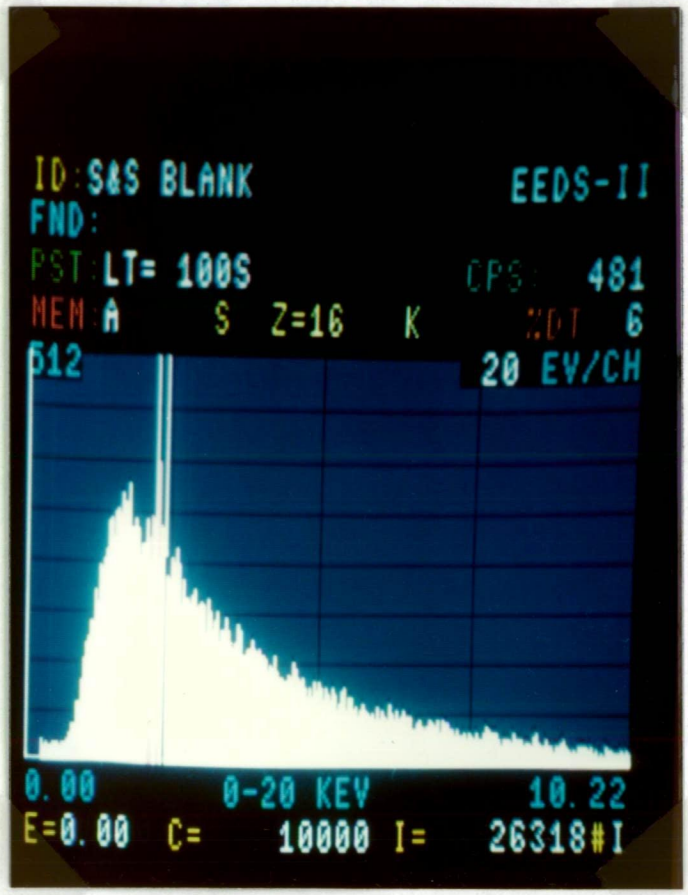
Figure 5.33 shows the EDAX spectra of a blank glass microfibre filter. Silicon is most predominant in the blankfilter among other elements including Al, Ca, Mg, K, Na, Ti, Zn, V, Cl, etc. The levels of impurities could vary from batch to batch of filters manufactured (Oikawa, 1977).

Figure 5.33. EDAX spectra of a blank Whatman GF/A glass microfibre filter, showing (from left to right) the presence of Na, Mg, Al, Si, K, Ca, Ti, possibly some Cl, and Zn.



Membrane filters, on the other hand, collect airborne particles predominantly on the surface (Perry and Young, 1977), and contain virtually no background impurities of trace metals, as shown by the EDAX spectra in Figure 5.34. The trace of sulphur shown was below detection limit. It could be due to impurity or caused by contamination during the preparation of the sample. Moreover, the membrane filter is more suitable for microscopic work than the glass microfibre filter (Perry and Young, 1977).

Figure 5.34. EDAX spectra of a blank Schleicher & Schull membrane filter, showing trace of sulphur which was below detection limit.



Consequently, only selected high-volume air samples collected by membrane filters were analysed by electron probe microanalyser operated at 15 kV with a beam current of 7×10^{-10} calibrated with a pure Cu sample. The airborne particulate samples were normally scanned for a 'window' area of 8 x 11 cm with 300 times magnification, but sometimes various 'window' sizes and magnifications were also used for identifying particles of particular interest. Additionally, spot mode was frequently used to pinpoint a particular particle so that its composition can be analysed.

(I) High-volume Air Samples

Figure 5.35 shows the EDAX spectra of a sample collected at Bell Bay Golf Club on 30 September 1983 from 1510 hours for 24 hours. The spectra of the elements shown are: Na (pale green), Al (yellow), S (pink), Cl

(dark green). Typical compositions of the sample (for 5 scans at different area of the sample) are shown in Table 5.59. Each element is analysed as oxides and, due to the shortcoming of the computer program set up for the instrument, elements like Zn and Cu are not included for the analysis. Thus the figures given in the table should be viewed in this perspective.

Figure 5.35 EDAX Spectra for a 24-hour sample collected at Bell Bay Golf Club on 30 September - 1 October 1983.

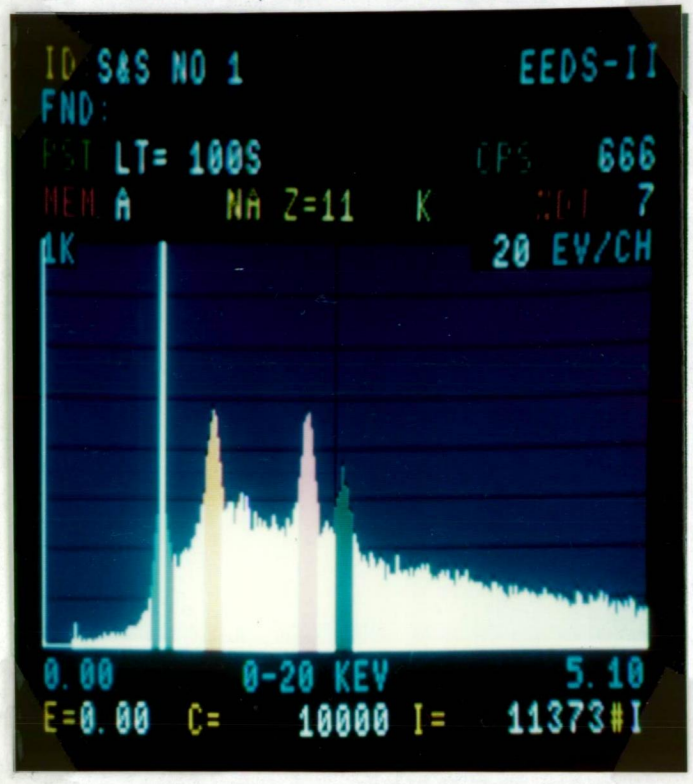


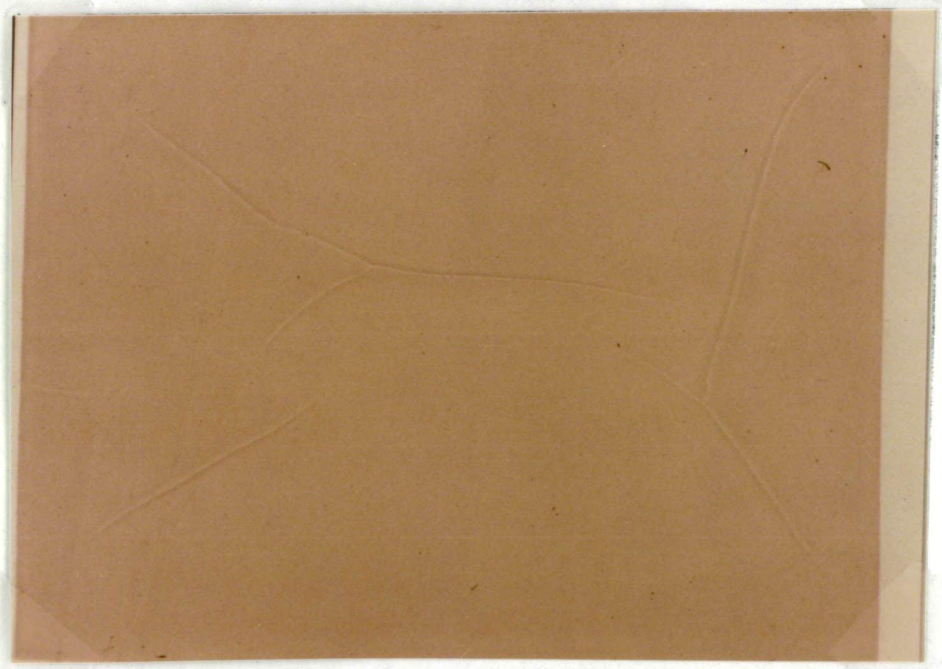
Table 5.59 Chemical Composition of a sample collected at Bell Bay Golf Club on 30 September - 1 October 1983. Five scans were made at different areas of the sample.

Composition/Scan	1	2	3	4	5
		(% weight of sample)			
SiO_2	0.10	0.09	0.10	-	-
Al_2O_3	0.50	0.51	0.55	0.52	0.51
Na_2O	0.45	0.46	0.49	0.49	0.48
SO_3	0.77	0.82	0.84	0.80	0.78
CL	0.21	0.24	0.23	0.21	0.27
Total	2.04	2.11	2.20	2.02	2.05

Of all elements analysed, S had the highest concentration (% weight) of the sample, and it was more likely to have come from the industrial area, particularly Comalco as NW wind was persistent throughout the sampling period. The rather high concentration of Al justifies this explanation. Only trace of Si was found, while Mn was below the detection limit.

It is interesting to examine the sample collected at Bell Bay Port Office at about the same sampling period (from 1545 to 1545 hours on 30 September - 1 October) (Figure 5.36).

Figure 5.36. A high-volume air sample collected at Bell Bay Port Office on 30 September-1 October 1983 using a membrane filter. The brown colour of the sample indicates a high loading of Mn.

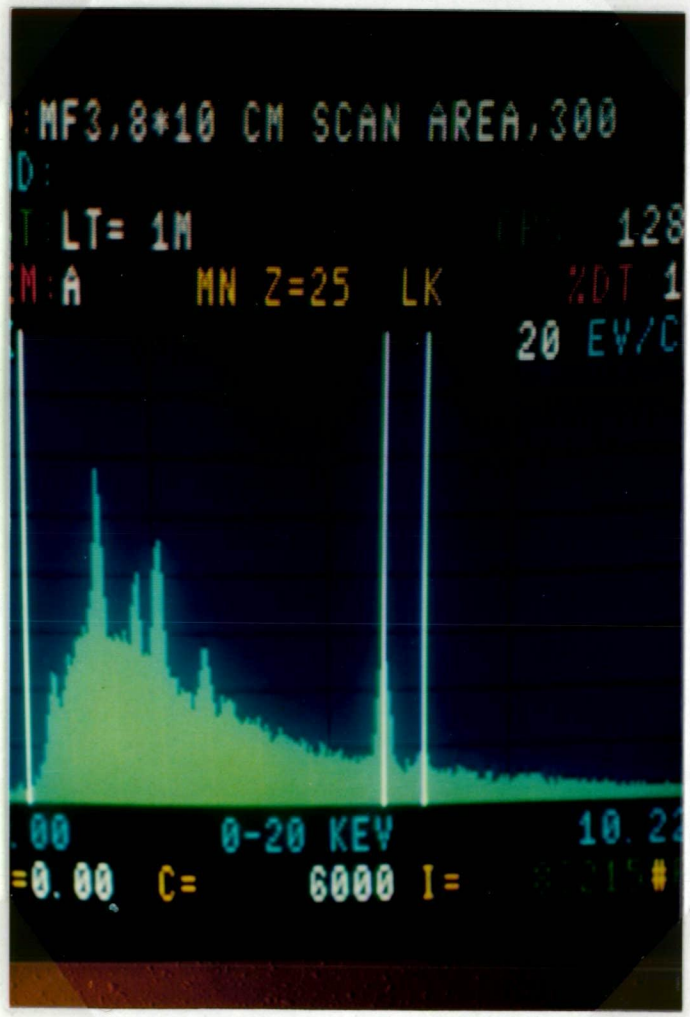


The composition detected for several scans at magnification 300X for a 'window' area of 8 X 10 cm are given in Table 5.60. The sample contained the highest concentration of Mn, followed by Si and S. Other elements detected included Na, Cl, K and traces of P and Mg. The high concentrations of Mn and Si and the low concentration of Al suggest that the location was strongly influenced by the air emissions from Temco rather than Comalco on this occasion, due to the prevailing NW wind during the sampling period. It appears that Temco is also a source of sulphur. Typical EDAX spectra for this sample are shown in Figure 5.37.

Table 5.60. The chemical composition of the sample shown in the above figure. Seven scans were made at different areas of the sample.

Composition/Scan	1	2	3	4	5	6	7
	(% weight of the sample)						
P_2O_5	-	-	-	-	-	0.12	0.11
SiO_2	0.92	0.81	0.79	0.93	0.83	0.80	0.79
Al_2O_3	0.23	0.18	0.20	0.32	0.17	0.17	0.21
MnO	1.54	1.43	1.35	1.56	1.49	1.55	1.43
MgO	0.24	0.22	0.19	0.19	0.21	0.19	0.18
K_2O	0.18	0.20	0.18	0.21	0.20	0.24	0.22
Na_2O	0.64	0.59	0.48	0.69	0.63	0.57	0.57
SO_3	0.69	0.67	0.66	0.68	0.68	0.66	0.66
CL	0.50	0.47	0.47	0.52	0.49	0.50	0.53
Total	4.95	4.58	4.32	5.09	4.71	4.80	4.70

Figure 5.37. EDAX spectra of a 24-hour sample collected at Bell Bay Port Office on 30 September - 1 October 1983. The peaks shown (from left) are: Na, Si, S, Cl, K and Mn respectively.



A magnified (300X) Mn-rich particle is shown in Figure 5.38. Spot mode analyses on this particle revealed that MnO accounted for 50-76% in the particle, while significant amount of K_2O (10-19%) was also present, with traces of Al_2O_3, P_2O_5, SiO_2, Na_2O, and MgO.

Figure 5.38. A Mn-rich particle in a sample collected at Bell Bay Port Office. Magnification 300X.

(II) Monthly Deposition Samples

As a matter of interest, a few of the monthly bulk deposition samples (water insoluble solids retained by a cellulose acetate filter of 0.45 µm porosity after filtration) were also analysed by SEM/EDAX, under the same operating conditions as described above. No background metal impurities in the blank of these filters were detected, though there was a trace of sulphur which was below detection limit (Figure 5.39). The analyses reveal the presence of some chemical elements which were not identified by flame AAS.

Figure 5.39. EDAX Spectra for a blank SM 111 cellulose acetate filter. Magnification 2500X.

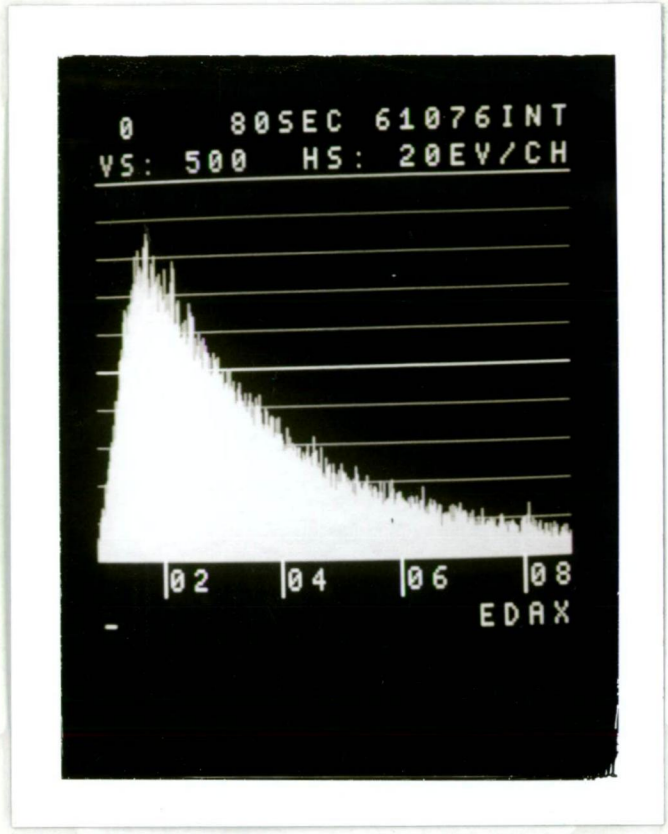


Table 5.61 shows the chemical composition of three samples collected in April 1983 at locations 3, 4 and 8 (See Figure 3.10 on page 76). The values, though obtained by scanning a 8 X 11 cm 'window' area with 300X magnification, are fairly typical for the sample analysed, as repeated scans on different areas of the sample produced similar results.

The analysis for the sample at location 8 shows the highest percentage weight (36.36%) of the sample, indicating that the sample (hence the location) was 'dustiest' compared with the other two locations. This is to be expected as location 8 was at the centre of the industrial area. The major composition in the sample at location 8 was predominated by Al (the concentration of which was about 5 and 17 times higher than those at locations 4 and 3), followed by Si (the concentration of which was comparable to that at location 4, but 2.6 times higher than that at location 3), and Mn (the concentration of which was about 26 and 21 times higher than locations 4 and 3). Thus the sources of these elements could be easily identified. These suggest the

strong influence of the air emissions from the two smelting industries on the location.

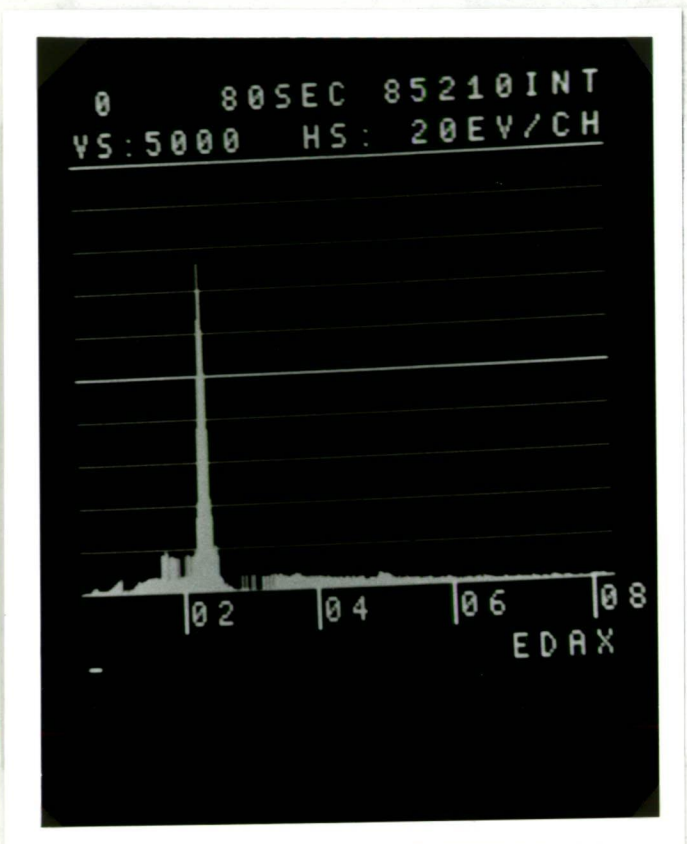
Table 5.61. Chemical composition of monthly bulk deposition samples (water-insoluble solids) collected in April 1983 at locations 3, 4 and 8 in the lower Tamar Valley.

Chemical composition	% by weight		
	Location 3	Location 4	Location 8
P_2O_5	0.06	1.43	1.05
SiO_2	3.33	8.42	9.65
TiO_2	0.16	0.20	0.42
Al_2O_3	1.09	3.40	17.31
V_2O_3	0.15	-	0.14
Cr_2O_3	-	-	0.16
FeO	0.99	0.90	2.25
NiO	-	-	0.18
MnO	0.20	0.16	4.09
MgO	-	-	0.27
CaO	0.07	0.30	0.18
K_2O	0.28	0.76	0.24
Na_2O	-	-	0.13
SO_3	7.63	1.20	0.31
Cl	-	0.11	0.05
Total	13.94	17.00	36.36

The sample at location 3 shows the lowest percentage weight of the sample for all elements analysed except S, which was about 6.4 and 2.1 times higher than those at locations 4 and 8. This appears to explain the very low pH (4.6) of this sample before filtration. As location 3 was only 0.8 km downwind (ESE) of the power station, it seems more logical to attribute the high level of S deposited at the location to this source than other sources. An EDAX spectrum of a S particle in this sample is shown in Figure 5.40.

It is also interesting to note the presence of other trace elements such as P, Ti and V at the locations. The figures in Table 5.61 suggest that Ti was contributed more from the industrial area, while traces of V and P could be contributed by the thermal power station and the metal smelting industries.

Figure 5.40. EDAX Spectra of a particle in monthly deposition sample collected at location 3 in April 1983, showing sharp spectrum of S.



Other elements which were not encountered at location 4 in the same month but present in the sample were Cr, Ni (presumably contributed by Comalco as these are found statistically correlated with Al and not Mn) (See Table 5.20 on page 333), and Mg (presumably contributed by the Pioneer cement mixing plant nearby).

5.12 Conclusions

The atmospheric deposition samples collected at 17 locations in the lower Tamar Valley from September 1982 to August 1983 were analysed. The mean deposition rates of water-insoluble dust ranged from 32.4 to 338.3 mg m^{-2} day^{-1}. For trace elements Al, F, Mn(total) and Fe, which were analysed using flame AAS, the mean deposition rates ranged from 445 to 5 638, 89 to 12 568, 38 to 3 676, and 392 to 1 534 μg m^{-2} day^{-1} respectively. Normalising the mean deposition rates to the intended

'background' levels (which were the lowest in all cases), the ratios vary from 1.2 to 12.7 for Al, 1.7 to 139.8 for F, 1.8 to 97.8 for Mn(total), 1.5 to 4.0 for Fe. In general, the fluxes of the trace elements were much higher within 3 km of their respective emission sources, but the air emissions from the two heavy industries could travel at least 10 km up the valley. The spatial variations of the deposition reflect the locality of the emission sources and the particle size distribution of the pollutants with respect to the meteorological conditions, in particular the wind vectors. Statistically, Al and F, as well as Mn and Fe (both insoluble) are found to be significantly correlated. The effects of the deposition of these trace elements to the local environment and ecosystems are difficult to assess, as no ambient air standards derived from similar sampling and analytical techniques are available for comparison.

The pH of the monthly bulk deposition samples (from July 1982 to August 1983) varied from 4.0 to 8.0, and from 4.3 to 5.8 for 17 event rain samples collected on 7-8 July 1984. The fluxes of hydrogen and excess sulphate ions are significantly correlated, with correlation coefficient r=0.94 at 0.1% significant level for acidic (pH < 5.6) bulk deposition samples from September 1982 to August 1983, and with correlation coefficient r=0.93 at 1.3% significant level for acidic event rain samples. The thermal power station appears to be the major source of acid-producing species, particularly sulphate, which could have caused the low pH of some deposition samples. The air emissions from the station could be transported over the Tippogoree Hills by the westerly airstreams.

Chemical speciation of precipitation samples by FT-IR was attempted. The major ions for acid-base equilibrium such as sulphate, nitrate and ammonium are identified, together with hydrocarbons. The technique seems to be feasible and promising. With a good reference library, it could be used as a complement of other elemental analytical techniques such as SEM/EDAX (for solids) and AAS (for solution) for the identification of chemical compounds.

The analyses of high-volume air samples show that the 24 hour concentrations of TSP and Mn in the Bell Bay industrial area could exceed 100 $\mu g\ m^{-3}$ and 10 $\mu g\ m^{-3}$ respectively. These are the ambient air

standards adopted by some advanced countries. Comparison of ambient air concentrations should be cautious unless similar sampling techniques (preferably with similar filters, or with filters of similar collection efficiencies) are used. No ambient air standards for Al are available. The concentrations of Al (tracer of air emissions from Comalco) and Mn (tracer of air emissions from Temco) depend largely on the locality and the prevailing wind conditions. Statistical analysis shows that the concentrations of TSP at Bell Bay Golf Club (about 2.5 km SE of Comalco) are significantly correlated with wind speeds (correlation coefficient r=0.77 at 3.7% significance level) provided the NW wind is persistent.

SEM/EDAX are also used to characterise the chemical composition of some selected high-volume air samples and monthly bulk deposition samples. The sources of the major trace elements such as Al, Mn, Si and S are identified. Analyses show that the location 0.8 km downwind (ESE) of the power station collected more S particles than the upwind locations. Comalco and Temco are also the sources of S particles.

5.13 Recommendations for Further Research

The ambient air monitoring in this study only represents a small part of the much needed and long-delayed air quality study in the lower Tamar Valley. The scope for further research in the study area is still very wide. The following aspects are considered to be important in relation to the industrial emissions from the Bell Bay area.

(1) The existing dust fallout monitoring programme undertaken by the Tasmanian Department of the Environment in the lower Tamar Valley does not seem to produce very useful results. The programme can be greatly improved if it is based on the extended network of this study. Apart from the monthly sampling technique, the new short term (3 to 24 hours) monitoring technique as developed by Williamson and Cantrell (1980) seems useful for the quantification of peak short term dustfall occurrences associated with varying meteorological and plant operating conditions.

(2) Regular and systematic high-volume air sampling should be undertaken, particularly within 3 km of the industrial area, so that the spatial and temporal variations of TSP and trace metals can be more comprehensively assessed. Polystyrene (or microsorban) filters, which have much lower blank concentrations of trace metals compared with glass

microfibre filters, and are not fragile as the membrane filters, can be used as an alternative filter (Ranweiler and Moyers, 1974; Oikawa, 1977).

(3) Continuous monitoring of HF (use of the major air pollutants from the aluminium smelter which was not measured in this study due to lack of equipment), SO_2, O_3, CO and NO_x (these were measured but no useful data were obtained because of frequent malfunctions of equipment) in ambient air and assessment of their concentrations under various meteorological conditions, in particular, the 'worst-case' conditions. This should be done as long as practicable so that representative data can be obtained.

(4) Wet-only deposition should be sampled regularly for further analyses so that the precipitation chemistry in the area can be better understood. Samples could be collected weekly, daily or on an event basis. Automatic wet-only samplers should be used to avoid any influence of dry deposition and also the contamination caused by bird-droppings.

(5) Dry deposition of various pollutants such as HF, SO_2 and metal particulates in the area should also be estimated by measurements.

(6) The technique used to speciate the chemical composition of the precipitation samples by FT-IR, as demonstrated in this study, is promising, but needs to be further developed, refined and consolidated. The technique can be applied for analysing the chemical composition of the stack emissions so that the sources of the pollutants at the 'receptors' can be readily identified.

Unless a good meteorological data base is supplemented by a good ambient air data base, the predictions of ground level concentrations of various pollutants under different meteorological conditions, by any mathematical model cannot be validated.

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Chapter 6 Towards A Better Air Quality Management

6.1 Is There An Air Pollution Problem?

The last four chapters attempt to assess the air quality in the lower Tamar Valley, based on the limited literature data, and on measurements of various meteorological and ambient air parameters.

So, is there an air pollution problem in the lower Tamar Valley?

This is the question of most concern to various interested parties and authorities, and one for which there is no straightforward answer.

Due to the various constraints of this study, only a short term rather than a much preferred long term assessment was possible. Additionally, the data were collected at a time when both Comalco and Temco rationalised their production programmes, particularly Temco which greatly reduced production, due to world recession. These considerations bring the representativeness of the data into question.

In spite of the fact that this study is only preliminary, some interesting aspects emerged. These are summarised and highlighted as follows.

(1) Perception by Local Residents

The public enquiry by the Senate Select Committee on air pollution in 1969 clearly reflected the perception and concern of the local residents with regard to the deterioration of air quality in the lower Tamar Valley, particularly at George Town, which is about 4 km NW of the Bell Bay industrial area. Evidence given included that from George Town Council which represents a population of 7000 in the area.

A brief perception survey among 66 local people at the beginning of this study shows that 71.2% of the respondents thought that there were air pollution problems in the area, particularly at Bell Bay, George Town, Low Head and Rowella.

(2) Vegetation Dieback

Vegetation dieback in the lower Tamar Valley became apparent in the early 1960s, and different theories have been given for the causes of this environmental deterioration (see Section 2.3.5, page 39-45). Davidson (1980), a former employee of the Tasmanian Forestry Commission, observed that "the severity of the dieback steadily increases as one travels north from the Batman Bridge reaching a peak in the hills east of George Town" and "the worst hit of the hills are: (1) the wooded hills at Low Head; (2) the Buffalo, George Town, Sugar Loaf and Mt George in the Mt George Range; and (3) the north western end of the Tippogoree Hills". Doley (1984) inspected the revegetated area of Comalco in February 1984. He observed that on one particular site along Bell Bay Road, the extent of visible injury on Pinus radiata decreased with increasing distance from the aluminium smelter, and the symptoms were most extensively developed on the south-eastern side of the trees. Doley also observed similar symptoms on a site near Lauriston Reservoir (about 2 km ESE of Comalco), particularly on the western side of the crown, where about half of the needles of the trees were injured. Doley believed that the injuries were more likely to be caused by fluoride (from a westerly located source) than sulphur dioxide (from an easterly located source). However, on the hillside north of Lauriston Reservoir, the one-year old juvenile leaves of E. globulus suffered from a variety of symptoms on different trees, and the injuries were more prominent on the south-eastern side of crowns than elsewhere.

It is possible to relate the affected areas as observed by Davison and Doley with the wind flow characteristics in the lower Tamar Valley area. Some of these areas (for examples, Low Head, the Buffalo, George Town and Bell Bay Road) are usually under the strong influence of S to SE drainage flows, which transport air emissions from Comalco, or Temco, or the thermal power station, or all, while others (for examples, Mt George and the northern end of the Tippogoree Hills) are affected by the SW and W winds which transport air emissions from Comalco or Temco, or both. While the site near Lauriston Reservoir is affected by the SW to W winds which transport air emissions from the industrial area, the hillside north of Lauriston Reservoir is more affected by the air emissions from the thermal power station carried by the SE drainage flows.

It is noted that during calm conditions in colder months, the SW katabatic winds originating from one of the larger valleys on the western shore (which accounted for 15% at mid-night to 11% at 0300 hours in winter 1983) could cross the river, spread out and reach the industrial area as light W to WNW winds. Drainage flows or katabatic winds are generally weak (< 2 m s^{-1}), and they could carry air pollutants from the industrial area in high concentration, and hence be more detrimental to the environment. Likewise, the NE katabatic winds originating from the saddle between Mt George and the Tippogoree Hills, and the E katabatic winds originating from the Tippogoree Hills could also transport the air pollutants from the industrial area to the Beauty Point-Ilfraville and Kelso areas where vegetation damage had been first reported in the early 1960s.

Wind data from station 3, which was closest to the two metal-smelting industries and the thermal power station, show about 11% of light winds (< 1.5 m s^{-1}), presumably mostly katabatic, occurred in autumn and winter 1983. About 22% of slight winds (1.6-3.3 m s^{-1}) of possible katabatic origin were also observed from mid-night to 0900 hours at this station.

Air pollutants such as fluorides are cumulative. Although the concentrations of these pollutants transported by the NW prevailing winds, which occurred more frequently during the afternoon and are much stronger than the drainage flows, may be small, long-term accumulation could cause serious damage to vegetation. Perhaps this explains the vegetation damage SE of the industrial area. Doley (1983) advocated that "the appearance of more extensive visible injury at greater distances from the (aluminium) smelter may be associated more with general exposure to wind than to fluoride itself". This view remains to be substantiated.

Apart from the NW and SE prevailing winds, the air emissions from the thermal power station are also influenced by the NE katabatic winds coming from the Tippogoree Hills. The stack of the power station (107 m above ground) is much higher than those of the two metal-smelting industries (38-40 m above ground), hence the air emissions could be carried much further away from the source, as evidenced by the analyses of acidity in the precipitation samples collected in remote areas.

(3) Fluoride Levels in Grazing Animals

Tests undertaken by the Department of Agriculture between 1968 and 1975 show that the fluoride levels in the urine of cattle in the lower Tamar Valley are about 5 to 15 times higher than the levels in a control location (Department of Agriculture, 1984). The highest concentration was found in Low Head, which could be related to the influence of S to SE down-valley flow. Bone ash tests conducted from 1981 to 1983 show that samples from Rowella and Greenhythe had higher fluoride levels, and these could be related to the influence of the NW prevailing winds.

(4) Foggy and Hazy Days

A total of 70 fog days (which occurred most frequently in colder months during the night) and 40 smoke haze days (which occurred most frequently in warmer months during the afternoon) were observed from July 1982 to December 1983 in the Bell Bay area. These reflect the number of days in which potential air pollution problems could occur. There have been many cases where heavy fogs and smoke hazes (visibility 100-200 m) were found to occur consecutively for two to three days. On one occasion, heavy fogs even occurred consecutively for a period of 4 days. The persistence of a fog event could last the whole day.

Fogs may be formed with aerosols or suspended atmospheric particulates acting as condensation nuclei. They are extremely good scavengers of atmospheric pollutants, perhaps better than rains or snows (Wisniewski, 1982). They could react with the acidic species such as HF, SO_4^{2-} and NO_3^- to form acidic fogs.

It may be interesting to note that 46 fog days were recorded at Bell Bay in 1983, which were twice as many as those recorded at Low Head Lighthouse, though the two locations are only about 10 km apart.

(5) Temperature Inversions

Temperature inversion occurs when air temperature increases with height (i.e. the temperature lapse rate is negative), hence creating very stable atmospheric conditions and suppressing vertical motion and turbulence (and hence mixing). Inversions in valleys are usually associated with air pollution problems if the air emissions are trapped

below the inversion layer. The break-up of surface inversion could result in fumigation and give rise to the greatest ground-level concentrations.

Based on the temperature difference between Mt George Lookout (180 m elevation) and Pt Effingham (10 m elevation) from December 1982 to July 1983, it is estimated (excluding 94 missed days) that there were 111 and 44 daytime and nightime inversions respectively (the ratio is about 2.5 to 1), with 13 occasions when daytime inversion was followed by nighttime inversion with a late afternoon break. Daytime inversions occurred most frequently in warmer months, particularly in summer, suggesting the strong influence of the incoming sea breezes. On the other hand, nighttime or radiation inversions occurred most frequently in colder months, especially in winter. An inversion could occur for a few hours in the morning, or night, or both in the same day, or it could last from the night to the following morning, and sometimes even afternoon, and the whole process could be repeated consecutively for a few days.

Limited tethered balloon soundings data in September and October 1982 show that the morning surface inversion layers, sometimes associated with the occurrence of the wind speed maxima, were able to develop up to a height of 200 m above the ground surface (40 m above sea level) where the tethered balloon was launched. This is also the height below which the wind field of the lower Tamar Valley is strongly influenced by local katabatic winds and S to SE down-valley flows in the mornings, and above which gradient winds prevail.

Surface inversions could be caused by the introduction of sea breezes. An elevated inversion layer at a height of 425-530 m above ground was observed in the industrial area during a sea breeze evening.

Whether the plume from the 107 m stack of the thermal power station could penetrate the inversion layers under various atmospheric stability conditions (Pasquill-Turner classes E, F, and G) remains to be investigated. However, it has been observed that, under stable atmospheric conditions, the plume failed to penetrate the ground-based inversion of height about 200 m, and bent towards the SW direction, possibly due to the influence of the NE katabatic winds originating from the Tippogoree Hills.

(6) Sea Breezes

In the Tamar Valley, NW sea breezes, which are more frequent than N or NE sea breezes, occurred about one in every three days in summer, about one in every five days in spring and autumn, and about one in every seven days in winter during the study period. The sea breezes could flush and dilute the air pollutants from various sources in the Bell Bay area. However, they also could carry the air pollutants further up the valley and possibly create air pollution problems. Air emissions from the industrial area could be trapped within a surface inversion layer caused by the sea breeze. It is possible that the air pollutants, including those from Launceston and Bell Bay, transported by the drainage flows to the coast in the morning, could be returned by sea breezes a few hours later in the day. Supplemented by current emissions, this could create smog problems and reduce air quality. Some of the smoke haze days, as discussed earlier, could result from these conditions.

(7) Upstream Blocking

Upstream blocking of NE winds channelled through the saddle between Mt George and Tippogoree Hills by the Asbestos/Dazzler Ranges on the western shore at a height of 100 m was found to have occurred. The blocking brought the air in the lower layers almost to a standstill. This phenomenon has major implications for air pollution problems in the lower Tamar Valley because once the air pollutants are emitted into the blocked air layer, little or no ventilation can be achieved.

(8) Atmospheric Deposition

Chemical analyses of the bulk (wet and dry) atmospheric deposition samples collected at 17 locations in the lower Tamar Valley from September 1982 to August 1983 show that the mean deposition rates of insoluble dust ranged from 32.4 to 338.3 mg m^{-2} day^{-1}. For trace elements Al, F, Mn(total) and Fe, the mean deposition rates ranged from 445 to 5 638, 89 to 12 568, 38 to 3 676, and 392 to 1 534 µg m^{-2} day^{-1} respectively. Normalising the mean deposition rates to the intended 'background' levels (which happened to be the lowest in all cases), the ratios vary from 1.2 to 12.7 for Al, 1.7 to 139.8 for F, 1.8 to 97.8 for

Mn(total) and 1.5 to 4.0 for Fe. In general, the fluxes of the trace elements were much higher within 3 km of their respective emission sources, but the air emissions from the two heavy industries could travel at least 10 km up the valley.

The impact of the depositional fluxes of the trace elements on the local environment and ecosystems is difficult to assess, as no ambient air standards derived from similar sampling and analytical techniques are available for comparison, at least in Australia. However, the upper limits of the mean deposition rates for these elements are certainly very high. As a reference, a deposition rate of 100 $\mu g\ m^{-2}\ day^{-1}$ is adopted as an ambient air standard for gaseous F (as HF for a 30 day period) by the South Carolina Pollution Control Authority (Rich, 1973). This may not be applicable to the lower Tamar Valley unless the figure is derived from similar sampling and analytical techniques.

(9) Acidity of Precipitation Samples

The pH of the monthly bulk deposition samples (from July 1982 to August 1983) varied from 4.0 to 8.0. Sixty one out of 194 samples (or 31.4%) were found acidic (pH < 5.6). Of these, 25 samples (or 12.9%) had pH < 5.0 (excluding contaminated or damaged samples). As the bulk deposition includes dry deposition which is mainly contributed by the larger alkaline species such as Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} rather than the acidic aerosol particles containing SO_4^{2-} and NO_3^{-}, it is probable that the actual number of acidic bulk deposition samples could be higher than that measured.

To put this into perspective, the pH of the monthly precipitation samples collected at the Cape Grim Baseline Air Pollution Monitoring Station for the same period was higher than 6.1 except for one sample, which had a pH of 5.75.

It appears that the locations along NW and SE of the thermal power station had higher frequency of collecting acidic samples, though there is evidence that the air emissions from the 107 m stack of the power station could be transported by the fresh to strong westerly airstreams over the other side of the Tippogoree Hills before rainout or washout.

The pH of the 17 event rain samples collected on 7-8 July 1983 ranged from 4.3 to 5.8, with 13 samples having pH < 5.6, and 4 samples

with pH < 5.0.

Statistical analyses show that the the fluxes of hydrogen and excess sulphate ions in both the bulk deposition and event rain samples are significantly correlated, suggesting that sulphate is the major acid-producing species. The power station is the major source of sulphate, though there are also some contributions from the industrial area, particularly from Comalco's anode baking plant.

(10) Concentrations of TSP, Al and Mn

The analyses of high volume air samples show that the 24 hour concentrations of TSP and Mn (tracer of air emissions from Temco) in the Bell Bay industrial area could at times exceed 100 $\mu g\ m^{-3}$ and 10 $\mu g\ m^{-3}$ respectively. These levels have been adopted by many advanced countries as ambient air standards. No ambient air standards for Al (tracer of air emissions from Comalco) are available, hence its impact on the physical and human environment is difficuilt to ascertain. The concentrations of Al and Mn depend largely on the locality and the prevailing winds.

Under surface inversion conditions when light SE winds were prevailing, the concentrations of TSP and Al at Mt George Motel and Low Head Lighthouse were much higher that those obtained under non-inversion conditions. On the other hand, the concentrations of TSP and Mn at Bell Bay Port Office were much higher when NW winds were persistent.

(11) Indicators for Air Quality

If the air quality can be assessed by the above indicators, the picture for the lower Tamar Valley is becoming clear: the industrial emissions undoubtedly have affected the environment in the area. Serious air pollution problems close to the industrial area could occur under certain meteorological conditions. However, further research is required before the impact of the air pollution problems to the environment can be fully assessed.

6.2 Towards A Better Air Quality Management

The air quality in an area is a function of many complex factors which include emission strength of various sources, air pollution control

(technically and legally), influences of meteorological parameters, and atmospheric chemistry.

While nature governs the meteorological parameters and atmospheric chemical reactions, people can improve the air quality through emission control. This has been the basis for regulatory control since the introduction of air pollution legislation or statute laws in many countries of the world.

So far as air pollution control is concerned, Tasmania has lagged far behind the other States. While Victoria, New South Wales, Queensland and Western Australia had their Clean Air Acts in 1958, 1961, 1963 and 1964 respectively, and South Australia its Clean Air Acts Regulations in 1969, Tasmania did not have the Environment Protection Act, the only legislation which has full control of air pollution, until 1973.

Prior to the enactment of the Environment Protection Act 1973, environmental control in Tasmania largely lay with the local governments and to some extent the Department of Health Services. "Although there is legislation covering various segments of environmental enterprise, most of this legislation is impossible to police or enforce" and "the means for environmental protection are both weak and scattered" (Chapman and Lake, 1972).

The Environment Protection Act 1973 was proclaimed to be "an Act to make better provision for protecting the environment of the people of the State". It provides adequate powers to the government which acts through the Minister for the Environment to control various aspects of pollution such as air, water and noise, as well as solid waste disposal. The Act is administered and enforced by the Department of the Environment under the auspices of the Director of Environmental Control who is directly responsible to the Minister. An Environmental Protection Advisory Council, which consists of both private and government parties, was set up to provide advice and recommendations to the Minister on environmental policy as well as pollution standards and emission controls which may be proclaimed as Regulations.

It is not intended to detail the environmental legislation here as this has been well discussed elsewhere (Fowler, 1982; Bates, 1983). However, the following points are considered relevant to the improvement of air quality in the lower Tamar Valley.

(1) There are no emission standards for Al and Mn particulates, two of the major air pollutants from the Bell Bay industrial area.

(2) The emission standards for F particulates and HF are based on volume concentration ($\mu g\ m^{-3}$) rather than mass of F in emission per unit mass of Al produced. Any dilution of the F emissions with a large volume of air would renders the emission test unrepresentative. Thus, the latter approach is considered to be more appropriate for emission control of these pollutants. Both SPCC of New South Wales and EPA of Victoria have adopted a standard of fluoride emission of 1 kg/tonne of Al produced for new aluminium smelters (Court and Ferrari, 1982). A similar standard is also recommended by the Australian Environment Council (AEC) and the National Health and Medical Research Counil (NHMRC) (AEC/NHMRC, 1986).

Emission limits of Al and Mn should also be based on the same approach.

(3) The sampling arrangement for emissions from roof ventilators in the aluminium smelter seems to be crucial. Different configurations of the cell roof ventilation have been found to produce different emission sampling results (Court and Ferrari, 1982). Therefore there is a need to standardise sampling methods for emissions from roof ventilators.

No emission testing for roof vents in Temco is known.

(4) There are ambient air standards for TSP (100 $\mu g\ m^{-3}$ for 24 hours) and HF (2.9 $\mu g\ m^{-3}$ for 4 hours, and 0.5 $\mu g\ m^{-3}$ for 90 days), but none for Al and Mn. As pointed out in a report by the United Nations (1979), the ambient air quality standard based on the mass concentration of TSP is rather poorly related to the actual pollutant burden on exposed individuals because the human respiratory system is more vulnerable to fine particulates (< 3 μm aerodynamic diameter) which can penetrate deep into the lungs. Moreover, the toxicological effects on human health depend largely on the specific chemical species of fine particulate material. Even if these particles are chemically inert, they can act as irritants and can impair lung function. Thus a systematic toxicological assessment of atmospheric aerosols based on physical and chemical parameters should be introduced.

While air quality standards are directed towards the protection of human health, there is also a need for ecological considerations to be taken into account (OECD, 1974).

(5) While Comalco has undertaken some environmental monitoring programmes, Temco has made no such commitments at all.

(6) Apart from the four monthly bulk deposition samples, the Department of the Environment does not monitor HF, SO_2, NO_x, CO, and O_3, suspended particulates or rain chemistry in the lower Tamar Valley. This seems to be unusual compared with the control authorities in the other states. Without monitoring data, enforcement of the Act would be impossible.

(7) The monthly bulk deposition samples are analysed for heavy metals, but no analyses of Al and F are included. The monitoring of fluoride concentration in vegetation is left to Comalco. In New South Wales, SPCC has undertaken the vegetation monitoring programme for more than 10 years in the Kuri Kuri area, and samples of representative Eucalypts have been taken at 3-monthly intervals from 15 sites.

(8) While the Director of Environmental Control may grant a licence to a "scheduled premise" such as Comalco or Temco conditionally or unconditionally or even refuse it "as he thinks fit" (S.25(1)), the Minister may exempt any person from complying with the provisions of some sections of the Act under Sections 15(7), 16(5) & 21(5) with regard to emissions. This makes the Act subject to political and economic influences and hence make its implementationn and enforcement more difficult. Both Comalco and Temco have exemptions for some emission which do not meet the regulatory limits.

(9) Air quality mathematical modelling has become a useful regulatory tool in many countries in recent years. In Australia, on the other hand, its potential applications in these areas have not been fully realised. In 1983, the Environment Protection Authority of Victoria proposed a plume calculation procedure to be evaluated for possible adoption as the approved calculation procedure in the State Environment Protection Policy (SEPP) for the air environment. Schedule E of the SEPP requires that an approved plume calculation procedure be undertaken to ensure that the maximum ground level concentration for any indicator or constituent does not exceed the specified design ground level concentration (Ross, 1983). There is no evidence that Tasmania will follow this trend in the near future.

Thus, it can be seen that there certainly is room for improvement as

far as air quality management in the lower Tamar Valley is concerned. A better air quality management not only relies on the good will of the government and industries, but also on more concerted efforts in air pollution control and research by the government together with the industries, supported by other interested parties such as the University and the general public. Environmental protection and management are the responsibility not only of the government and those whose activities are likely to pollute, degrade or damage the environment, but of the public. Thus public participation in the environmental protection process is necessary if confrontation between government and industry on the one hand, and the general public on the other, is to be avoided.

It is also necessary to enforce the environmental legislation, as well as to continue to improve and update various emission and ambient air standards if environmental quality is to be improved and maintained. Mr. J.F. Pottinger, the former Director of Environmental Control in Tasmania pointed out in a conference held in Canberra in 1973:

> "In order that environmental legislation should be effective it must be reasonable, enforceable and based as far as possible on scientific data. Perhaps more importantly it must be enforced. This means that trained staff must be made available with adequate supporting facilities. Legislation is useless unless implemented competently."

Perhaps this should be regarded as the first step for a better air quality management in the lower Tamar Valley, and indeed, in any industrial area in Tasmania.

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APPENDICES

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2. LOW, P.S and TODD, J.J., 1984; A Preliminary Study of Air Quality in Bell Bay, Tasmania, in: Hartmann, H.F., O'Heare, J.N., Chiodo, J., and Gillis, R. (eds); Proceedings of Eighth International Clean Air Conference, Volume 2; the Clean Air Society of Australia and New Zealand, Melbourne; pp. 751-766.

3.* LOW, P.S., 1985a; Surface Wind Statistics for the Tamar Valley, Tasmania, I. Wind Roses, November 1982 - December 1983, Research Report No. 1, Air Quality Study Programme, Environmental Studies Research Project No. 6; Centre for Environmental Studies, University of Tasmania, Australia.

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6. LOW, P.S. and BLOOM, H., 1986; Atmospheric Deposition in the Lower Tamar Valley, to be presented at 7th World Clean Air Congress and Exhibition of the International Union of Air Pollution Prevention Associations, Sydney, Australia - 25-29 August 1986.

* N.B. Only the journal paper and the two conference papers (one co-authored with Dr J.J. Todd, the other with Professor H. Bloom) are attached. The three research reports are too voluminous to be included in the thesis, so a brief outline of the reports given in the mail order form is attached here for reference.

DUST AND HEAVY METALS FALLOUT IN HOBART AND ITS ENVIRONS, TASMANIA — A SUMMARY OF 8-YEAR MONITORING DATA.

Low Pak Sum

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ABSTRACT Dust and heavy metals fallout data have been published by the Tasmania Department of the Environment since 1973. However, these data have not been analysed in detail. This paper summarises and discusses these data with a view to providing some ideas about the air quality in the Hobart metropolitan area. Although the dustfall rates were found to be low (i.e. mostly less than 100 mg m^{-2} day^{-1}), the concentrations of the heavy metals, particularly those of zinc, iron, lead, manganese and copper in some suburbs were very high. The effects of these heavy metals on the local population and their environment have yet to be assessed.

INTRODUCTION Those who would like to know more about air pollution in Tasmania will soon find that it is quite difficult to gain a clear picture from the available literature. In fact, very little information on air pollution in Tasmania was published particularly before the mid-1970s (*1*). The Department of the Environment, Tasmania has accumulated some survey data on air pollution, especially on dustfall, since its establishment in 1972; however, these data are largely unanalysed and hence are not very accessible to the general public (*1*). Among the very few researchers who have made their contributions to the study of air pollution in Tasmania during the last few years, Professor H. Bloom* of the Chemistry Department in the University of Tasmania is most notable. For example, he has led the study of lead concentrations in the blood of children and some adults of southern Tasmania (*2*). Together with his students, Professor Bloom has modified and improved the techniques of sampling and analysing the airborne metals in particulate matter (*3,4,5,6,7,8*). He has also studied, with the staff members of the Department of the Environment, the distribution of heavy metals in the dust fallout in suburban areas of Hobart (*9*) and lead emissions from motor vehicles, mining and other sources (*10*).

The aim of this paper is to summarise and discuss the dust and heavy metal fallout data for the Hobart metropolitan area. These data have been published in the annual reports prepared by the Department of the Environment since 1973.

YARDSTICKS FOR DUSTFALL LEVELS The dust fallout in Tasmania was collected monthly by the conical glass funnel (nominal diameter 150 mm) and bottle (4.5 litre) type deposit gauge which has been widely used in Australia. It must be noted that the deposit gauge, while simple and economical, has a few limitations. These have been discussed by Low (*11*).

As there are no legal limits or guidelines on dustfall rate in Tasmania, it is difficult to assess the adverse effects of dust pollution at each sampling location. Some guidelines have been provided both in overseas and other states in Australia. For example, Williams and Edmiston (*12*), after studying the air quality in metropolitan Nashville, USA, recommended a maximum permissible dustfall level of 130 mg m^{-2} day^{-1} (averaged over a year), based on the figure for the water insoluble components. Dr. S. R. Craxford of the British Warren Spring Laboratory believes that the average urban grit and dustfall of 113 mg m^{-2} day^{-1} is a minor drawback of town life; a figure exceeding 200 mg m^{-2} day^{-1} makes a locality "unpleasantly dusty"; and a figure about 300 mg m^{-2} day^{-1} indicates "gross pollution" (*13*). Cantrell, Edwards and Williamson (*14*) have selected the upper acceptable limit of dustfall (water insoluble fraction) for residential areas to be 130 mg m^{-2} day^{-1} in their Portland cement dustfall study in Geelong, Victoria. They recommended that "the goal of urban planning authorities should be dustfall no higher than this level in order to guarantee the comfortable enjoyment of life or use of property".

The Department of Public Health of Victoria in 1966 suggested certain typical dustfall figures for various areas (*14*), as shown in Table 1. These are also followed by the Air Quality Section of the Department for the Environment in South Australia (*11*).

Table 1. Typical Dustfall Figures in Various Areas.

Classification	Dustfall (Water Insoluble Solids) mg m^{-2} day^{-1}
Rural	13 — 65
Residential	40 — 90
Light Industrial	100 — 160
Heavy Industrial	200 — 350

After consideration of many recommendations and suggestions, and based on his dustfall study in Adelaide, Low (*11*) proposed that a dustfall figure (water insoluble components) in excess of 100 mg m^{-2} day^{-1} be considered "slightly dusty". When a figure in excess of 120 mg m^{-2} day^{-1} is found in a residential area, it would be considered "moderately dusty" and likely to draw complaints from the residents. At 140 mg m^{-2} day^{-1}, the area would be regarded as "very dusty" and expected to draw heavy complaints from the residents. These figures, however, could only be used as yardsticks to measure the relative degree of dust pollution in a residential area and by no means should be regarded as "standard". It must also be noted that for dustfall figures at different locations or countries to be comparable, similar dust collectors and collection methods must be employed, preferably in similar climatic conditions. It has been found that the collection efficiency of a deposit gauge could vary with the design of the gauge and climatic conditions (*15*).

*Professor H. Bloom who retired at the end of 1981, is still actively engaged in research activities at the University of Tasmania.

SAMPLING LOCATIONS Dust fallout data of seven sampling locations in the Hobart metropolitan area were reported for the period July 1972 to June 1973 (*16*), and most of these sampling locations were still under the care of the Department of Health Services before full responsibility of air pollution monitoring was transferred to the Department of the Environment (*16, 17*). After the appointment of an Air Pollution Officer in June 1973, the sampling network was greatly extended and a total of 21 deposit gauges was established at various suburban sites. However, only five locations remain since July 1977 due to the "rationalisation" of the dustfall sampling programme (*16*).

Figure 1 shows all the past and present sampling locations in the Hobart metropolitan area and its environs. It is difficult, if not impossible, to describe the physical environment of the 16 phased out sampling locations. However, of the five currently operating locations, W1B, situated within the premises of the Hydro-Electric Commission (H.E.C.) substation at Risdon, is closest to the Electrolytic Zinc Works which was established in 1916. W3 is situated in Moonah, a mixed residential, commercial and industrial area in the Hobart metropolitan area. W8, about 24 km south-west from the city of Hobart, is also located within the premises of the H.E.C. substation at Electrona next to which was a calcium carbide plant. E1 and E2 are located on the eastern shore of the Derwent River, with E1 about 700 m on the north-north east of the zinc works and E2, about 2 km south-east from the zinc works. Both the dust deposit gauges at W1B and W8 are placed on the top of a steel stand about 1 metre above the ground, while the other three are placed on the top of garage roofs of heights greater than 3 metres. Although the deposit gauges at W1B and W8 are placed at a height comparable to the British Standard (1.2 m or 4 ft) (*18*), the height is half the minimum (i.e. 8ft or 2.4 m) recommended by the U.S. Air Pollution Measurement Committee (APMC) (*19*).

The APMC also recommended that the top of the dustfall container should be a minimum of 4ft (1.2 m) above any other surface such as a roof (*19*). This recommendation was not observed for locating W3, E1 and E2. However, all sampling locations are either free or reasonably free of interference from trees.

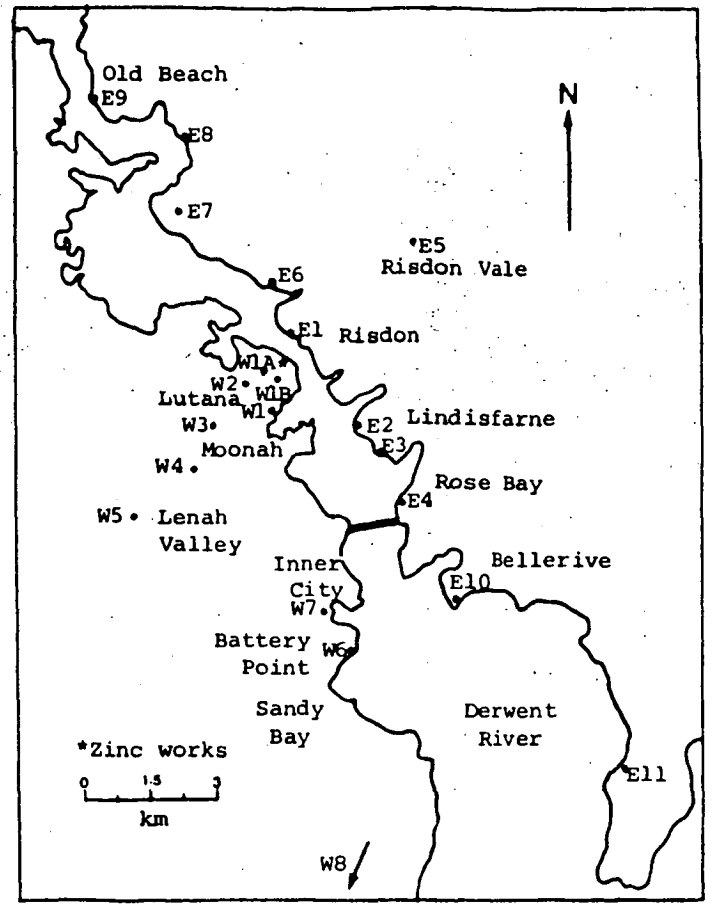

Figure 1. Past and present dust fallout sampling locations.

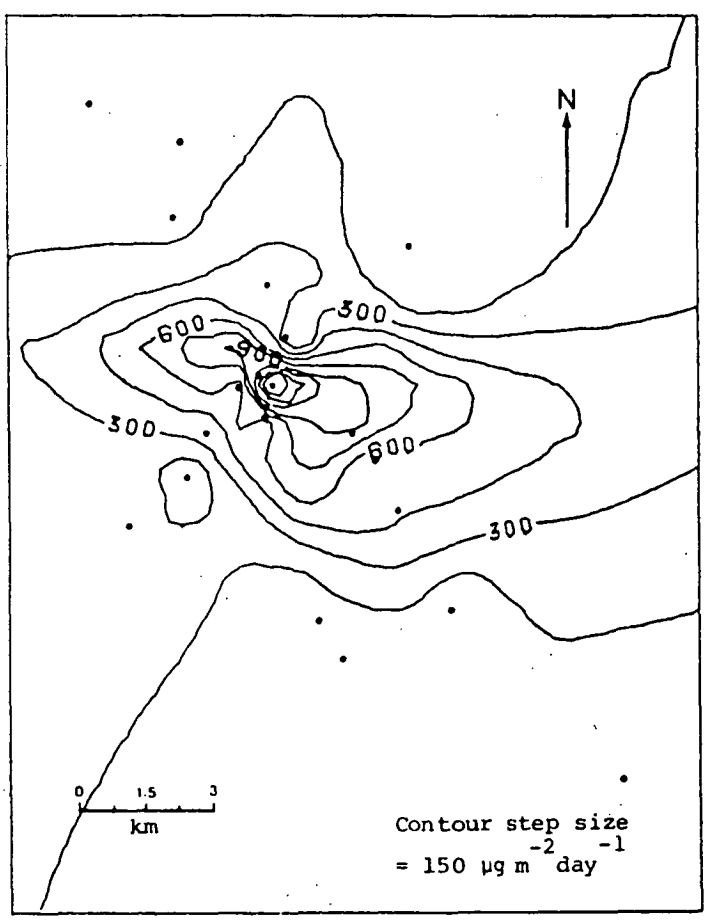

Figure 2. Four-year average of zinc fallout in Hobart metropolitan area (from 1973-1974 to 1976-77).

SUMMARY OF DATA AND DISCUSSION

(A) From 1973-74 to 1976-77*

Table 2 summarises the 4-year average dust and heavy metals† fallout rates for the 21 locations monitored from the year 1973-74 to 1976-77. A close examination of this table reveals that:

(1) the 4-year average dustfall rates varied at each location. This was to be expected because the dustfall rates were obviously influenced by such factors as the wind speed and direction, the rainfall, the topography of the location of the deposit gauge, the traffic, the dust particle size, the distance from the sources of emission and the rate of emission, etc;

(2) the average dustfall rates for all locations were lower than 100 mg m^{-2} day^{-1}, except for the location in Kalang Avenue (Lenah Valley) which had an average value of 118.3 mg m^{-2} day^{-1};

(3) the sampling locations on the western shore of the Derwent River were generally more dusty than those on the eastern shore;

(4) although the average dustfall rates at most locations were low, the levels of zinc in the dust fallout samples were high, particularly at the locations close to the zinc works (for example, W1A and W1B);

(5) W1A and W1B were two of the sampling locations closest to the zinc works, separated by a distance of less than 400 metres. While W1A had the highest average levels of zinc (1579.5 μg m^{-2} day^{-1}) and manganese (972.9 μg m^{-2} day^{-1}) and the second highest average levels of lead (221.6 μg m^{-2} day^{-1}), copper (22.1 μg m^{-2} day^{-1}), cadmium (8.4 μg m^{-2} day^{-1}) and cobalt (4.9 μg m^{-2} day^{-1}), W1B had the highest average levels of lead (302.1 μg m^{-2} day^{-1}), copper (27.6 μg m^{-2} day^{-1}), cadmium (9.9 μg m^{-2} day^{-1}), cobalt (19.4 μg m^{-2} day^{-1}), chromium (3.6 μg m^{-2} day^{-1}), Ni (2.1 μg m^{-2} day^{-1}) and second highest average levels of zinc (1544.0 μg m^{-2} day^{-1}), and manganese (600.2 μg m^{-2} day^{-1}). It is obvious that both the locations at W1A and W1B and their immediate environment were seriously affected by the heavy metals fallout from the zinc works;

(6) on the eastern shore of the Derwent River, the average levels of zinc at E2, E3 and E4 were higher than those at E1. As E2, E3 and E4 were downwind from the zinc works it was highly probably that the particulates deposited at these locations were transported from the zinc works by the north-westerly

*The sampling year ended at the end of June.

† The heavy metals in the dust fallout samples were analysed by using the atomic absorption spectrophotometry (AAS) technique.

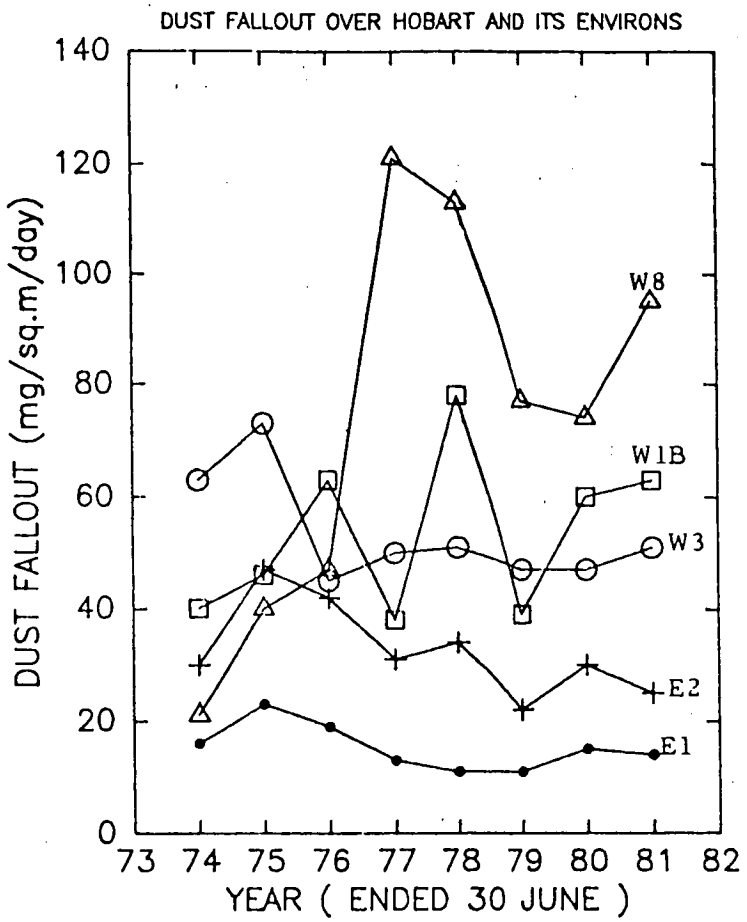

Figure 3. Dust fallout at 5 existing locations in Hobart metropolitan area and its environs.

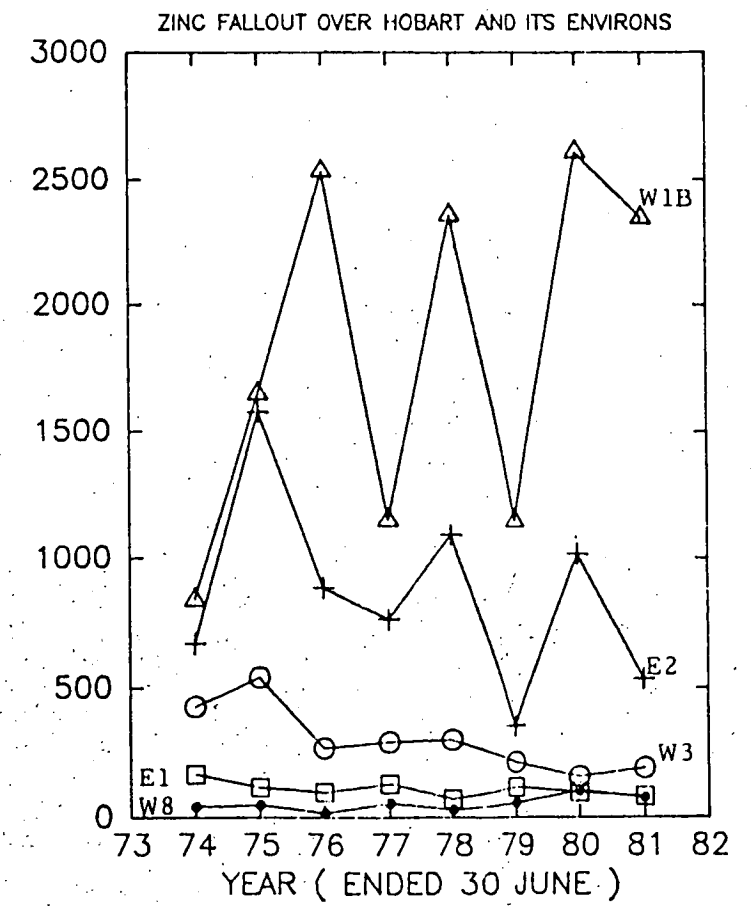

Figure 4. Zinc fallout at 5 existing locations in Hobart metropolitan area and its environs.

winds which are predominant during most times of the year. Similarly the average levels of zinc at E6, E7, E8 and E9 were higher than those at E1. As E6, E7, E8 and E9 were upwind from the zinc works, it was highly probable that the particulates deposited at these locations were transported from the zinc works by the south-easterly sea breezes which are predominant in summer afternoons;

(7) in general, the average levels of zinc decreased as the distance increases from the zinc works. This was true for the sampling locations on both shores of the Derwent River;

(8) apart from zinc, most locations also indicated a significant amount of iron, lead, manganese and copper, especially at locations close to the zinc works and those downwind or upwind from the zinc works. It seems that the heavy metals could be transported as far as several kilometres from the zinc works. It is also noted that the average levels of iron at all locations were higher than those of most other metals. This could possibly be due to the higher background level of iron compared with other metals.

The distribution pattern of the average zinc fallout in the Hobart metropolitan area from 1973-74 to 1976-77 is shown in Figure 2. The contours were drawn by a Zeta 1453 drum plotter, using the Surface II graphic system available at the Computing Centre in the University of Tasmania based on the data in Table 1. As was expected, the highest zinc fallout levels were concentrated at areas close to the zinc works. It is also obvious that the suburb Lindisfarne has the highest zinc fallout levels on the eastern shore. The distribution pattern of the zinc fallout was somewhat influenced by the north-westerly winds which channel down the Derwent Valley. The westerlies, easterlies and south-easterly sea breezes also appeared to have some effects on the distribution of zinc fallout from the zinc works.

(B) From 1977-78 to 1980-81

Table 3 summarises the average dust and heavy metals fallout rates for the remaining five sampling locations in the last four years of the analysis period. Except E2 which was shifted about 100 m further from the zinc works in mid-1978 and hence should

Table 2 Four Year Average of Dust and Heavy Metals Fallout in Hobart and its Environs, 1973-74 to 1976-77

Deposit Gauge Number	Location	Total Insoluble Dust ($mg\ m^{-2}day^{-1}$)	Heavy Metals ($\mu g\ m^{-2}day^{-1}$) Cd	Cu	Zn	Pb	Cr	Mn	Fe	Co	Ni
E9	Opposite Austin's Ferry, Old Beach Road	49.6	0.7	7.5	101.8	15.8	1.2*	8.0	915.0	0.9	1.1
E8	Opposite Cadbury's, Old Beach Road	29.6	1.0	8.4	134.0	13.5	0.6	5.4	265.0	0.6	0.5
E7	Derwent Laken Estate, Old Beach Road	22.9	1.0	11.2	129.0	22.7	0.8	6.9	388.0	1.0	0.6
E6	South End of Old Beach Road	40.2	1.7	7.5	315.1	29.4	0.7	12.1	895.0	1.7	0.7
E5	Linden Avenue, Risdon Vale	21.5	0.2	5.2	62.4	6.0	0.5*	3.2	413.0	0.5	0.6
E1	Esplanade, East Risdon	17.6	0.8	7.4	125.7	13.7	0.7	11.9	390.0	1.2	0.6
E2	Derwent Avenue, Lindisfarne	37.6	5.1	18.8	974.1	91.9	1.1	61.6	1060.0	9.3	0.7
E3	Lanrick Court, Lindisfarne	32.0	2.7	12.3	493.6	48.6	0.7	25.9	633.0	4.8	0.7
E4	Esplande, Rose Bay	66.4	2.2	10.7	451.6	47.1	0.7	21.0	678.0	3.3	0.9
E10	Abbotts Street, Bellerive	23.4	0.7	4.6	104.5	16.2	0.7	6.4	560.0	0.8	0.6
E11	Transmere Road, Transmere	25.9	0.4	6.6	89.0	12.5	0.4	5.8	485.0	0.5	0.5
W5	Kalang Avenue, Lenah Valley	118.3	0.7	12.2	190.8	31.8	2.0	17.8	1833.0	0.9	1.7
W4	Sinclair Avenue, Moonah	39.6	0.3	6.0	85.3	16.5	0.7	13.2	690.0	0.6	0.8
W3	Gormanston Road, Moonah	58.0	1.1	13.0	382.3	64.0	2.2	22.8	1583.0	1.6	2.2
W2	Bowen Road, Lutana	89.1	1.8	15.8	476.9	49.5	1.2	55.5	2400.9	2.9	1.7
W1A	Birch Road, Lutana	41.6	8.4	22.1	1579.5	221.6	1.5	972.9	1305.0	4.9	1.2
W1B	H.E.C. Risdon	46.7	9.9	27.6	1544.0	302.1	3.6	600.2	2655.0	19.4	2.1
W1	Risdon Road, Lutana	32.2	3.9	15.0	556.6	96.9	1.1	146.2	835.0	4.6	1.1
W7	Murray Street Wharf	38.0	0.6	9.2	124.1	45.7	1.3	20.6	1163.0	0.7	1.2
W6	Clarke Avenue, Battery Point	26.1	0.5	11.0	103.9	39.0	0.8	8.9	510.0	0.6	0.7
W8	H.E.C. Electrona	57.0	0.3	5.5	39.2	6.0	0.9*	17.5	613.0	0.8	1.6

* 3-year average

Table 3 Four Year Average of Dust and Heavy Metals Fallout in Hobart and its Environs, 1977-78 to 1980-81*

Deposit Gauge Number	Location	Total Insoluble Dust ($mg\ m^{-2}day^{-1}$)	Heavy Metals ($\mu g\ m^{-2}day^{-1}$) Cd	Cu	Zn	Pb	Cr	Mn	Fe	Co	Ni
E1	Esplanade, East Risdon	12.8	0.7	2.5	90.5	14.9	0.4	4.7	287.5	1.1	0.4
E2†	Ambleside, Lindisfarne	25.7	6.9	15.5	635.4	83.8	0.7	29.9	766.7	12.2	0.4
W3	Gormanston Road, Moonah	55.9	0.7	7.1	213.8	38.9	2.2	16.0	1040.0	1.1	0.9
W1B	H.E.C. Risdon	53.2	16.4	50.6	2115.8	482.0	4.9	619.2	3357.5	19.7	1.6
W8	H.E.C. Electrona	81.2	0.6	3.5	65.1	6.8	1.0	42.0	800.0	0.5	1.4

* Several errors have been discovered in the published dust and heavy metals fallout data as reported in the year 1977-78 and 1978-79. But these have been rectified by Low *(1)*.

† The sampling location E2 was shifted from Derwent Avenue, Lindisfarne to Ambleside, Lindisfarne in mid-1978. However, the new and old locations were only about 100 m apart. The values recorded for E2 in this table were the 3-year average values from 1978-79 to 1980-81.

be regarded as a "new" location, all the other locations were operated as before.

Of the five sampling locations, W8 had the highest average dustfall rate (81.2 $\mu g\ m^{-2}\ day^{-1}$) and lowest average level of zinc fallout (65.1 $\mu g\ m^{-2}\ day^{-1}$). The relative high dust fallout at W8 was probably caused by the carbide plant nearby.

Of course it would be difficult to assess the air quality of Hobart metropolitan area and its environs with only five sampling locations and hence limited results. However, comparing the results in Tables 1 and 2, it is interesting to note that both the average levels of dust and heavy metals fallout at W1B, the sampling location closest to the zinc works, were higher in 1977-78 to 1980-81 than those levels in 1973-74 to 1976-77. This raises the question of effective air pollution control, both legal and technological, in the past eight years.

Figures 3 and 4 show the dust and zinc fallout of the remaining five sampling locations from 1973-74 to 1980-81. There were, in fact, two sets of values for Lindisfarne, one for Derwent Avenue, Lindisfarne (before mid-1978) and the other for Ambleside, Lindisfarne (after mid-1978). For convenience, these two sets of values were plotted together under the general name of Lindisfarne.

The dust fallout trends at these five locations did not seem to match the zinc fallout trends, indicating that the sources of dust emission could be multiple. For example, the dust fallout rates at the sampling location in Gormanston Road, Moonah (W3) were higher than that at H.E.C. Risdon (W1B) in most years (Figure 3), yet the zinc fallout levels at W3 were much lower than that at W1B for all years since 1973-74 (Figure 4). It is also noted that while the dustfall rates at H.E.C. Electrona (W8) were generally the highest compared with the other four locations, the zinc fallout levels at this location were the lowest in almost every year. It is likely that the relatively high dustfall rates at W8 were contributed by the operation of a carbide plant nearby rather than any other sources. The dustfall rates at W8 fluctuated rather significantly from 1975-76 to 1978-79 while those at the other four sampling locations only varied slightly from year to year. The zinc fallout levels at H.E.C. Risdon (W1B) and Lindisfarne (E2) also fluctuated considerably compared with the other three sampling locations.

Low (*1*), who expressed the concentrations of the heavy metals in terms of micrograms per gram of the total insoluble dust (i.e. $\mu g\ g^{-1}$) for the above five remaining sampling locations from 1973-74 to 1979-80, found that some suburbs in the Hobart metropolitan area were constantly exposed to 10,000 — 40,0000 $\mu g\ g^{-1}$ of zinc, 10,000 — 80,000 $\mu g\ g^{-1}$ of iron, 10,000 — 20,000 $\mu g\ g^{-1}$ of manganese, 5,000 — 10,000 $\mu g\ g^{-1}$ of lead, 100 — 1,000 $\mu g\ g^{-1}$ of copper, 10 — 700 $\mu g\ g^{-1}$ of cobalt, 10 — 300 $\mu g\ g^{-1}$ of cadmium, 10 — 90 $\mu g\ g^{-1}$ of chromium and 10 — 70 $\mu g\ g^{-1}$ of nickel.

Ayling and Bloom (*9*), basing their comments on a typical monthly analysis, found that dust from the zinc-refining works had spread "many km across Hobart suburbs" and that "changes in average wind speed and direction significantly alter the pattern of distributed dust". Goodman, Noller, Pearman and Bloom (*20*), who obtained data from high volume air sampling at a site in Sandy Bay for fourteen weekly periods during 1971 to 1975, also found that "some heavy metals (cadmium, zinc and lead) in the Hobart atmosphere are not greatly different from values found in American cities."

CONCLUSIONS The dustfall rates in Hobart metropolitan area and its environs since 1973-74 were generally low, mostly less than 100 mg $m^{-2}\ day^{-1}$, the "slightly dusty" level as proposed by Low (*11*). It appears that the sampling locations on the eastern shore of the Derwent River were generally less dusty than those on the western shore.

The levels or concentrations of heavy metals, especially those for zinc, in the dust fallout samples were very high. In general, the levels or concentrations of zinc decreased with the distance of the location of the zinc works.

b Heavy metals particulates appeared to spread several kilometres across Hobart suburbs. The effects of these heavy metals on the local population and their environment, in particular, vegetation and possibly aquatic ecosystems, are virtually unknown. There is an urgent need for research on these aspects.

It is believed that the present five dustfall sampling locations are inadequate to cover the whole Hobart metropolitan area and its environs. In order to assess better the levels of suspended particulates in the ambient air environment, high volume sampling should also be undertaken frequently in the areas where there are known sources of air pollution. Micro-air sampling techniques as adopted by Noller and Bloom (*4*) are very useful as they provide a unique means for measuring very high concentrations of toxic metal particulates over short time intervals and in confined spaces (*8*).

A comprehensive study of the local meteorological conditions particularly the wind and temperature profiles in the lower atmosphere is also required. This should include a continuous wind monitoring programme near the zinc works, the major source of heavy metals fallout, so that the distribution patterns as well as the dispersion characteristics of these heavy metals from the source can be better understood.

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ANNOUNCEMENTS

Discount on Books for Members

Books published by Butterworths (which includes the Ann Arbor Science label) advertised in the Journal, are now available at a discount of 15 per cent to members of the Society and Journal subscribers.

Details of the publication/s required together with a cheque or money order for 85 per cent of the list price, made payable to the Clean Air Society of Australia and New Zealand should be sent to the Circulation Manager, P.O. Box 191, Eastwood, NSW, 2122, Australia. Publications will be forwarded direct by mail from Butterworths.

It is hoped that members will take full advantage of this new service.

BOOK REVIEWS

The Design of Air Quality Monitoring Networks R. E. Munn
MacMillan Publishers Ltd., 1981,
PRICE 20.00 pounds stg.

This small volume is the second of a series on air pollution problems under the Series Editorship of Dr. David Moore, known to many as an executive editor of *Atmospheric Environment*.

In these days of proliferating air pollution literature, it is pleasant to come across a volume of a size which one can with profit comfortably read from cover to cover without excessive expenditure of time. In a little over 100 pages the author has indicated ways in which one might approach the difficult task of providing the best configuration for a network of monitoring stations whose purpose is to produce information for a specific problem. Generally the theoretically ideal number of monitoring sites is well beyond what is practically possible because of capital and stopping restraints and the system must be optimised. The review of an existing network of long standing with a view to thinning out stations without loss of information or perhaps reallocation of stations to get additional information is another problem area. Both these topics are given considerable coverage with useful references.

The opening chapters cover briefly the historical aspects, the objectives of monitoring and the time and space variability of air quality. Then follows a chapter on the siting requirements for a single station, and a long chapter on methods available for network design. Three small chapters on miscellaneous related topics and practical guidelines follow.

Condensing the available information has naturally meant discarding a lot of detail, but the many factors which must be taken into account in work of this nature seem to be well covered. It is a volume that is recommended both for students and for people associated with monitoring networks.

J. O'HEARE

Air Pollution Chemistry
J. D. Butler
Academic Press Inc. (London)
Price: $52.50

This book provides a broader coverage of the interface between chemistry and air pollution than most other publications purporting to cover the area, which generally limit themselves to chemical interactions in the atmosphere. In this publication the only major area where chemistry has relevance to air pollution that is omitted is air pollution control. The depth at which topics are covered varies, but for the topics on which the author has concentrated there is a wealth of detail, data and current reference. These topics include human health effects, the levels of combustion-related emissions and the mechanisms of their formation, analytical techniques for polynuclear hydrocarbons, and all aspects of the chemistry of photochemical smog formation including the role of sulphur dioxide. The book ends with a useful discussion of urban atmospheres and their chemical composition. A surprising omission is the formation and effects of acid rainfall.

"Air Pollution Chemistry" would be a good introduction for a chemist interested in the applications of chemistry to air pollution problems, and a useful reference text to those undertaking air pollution studies at undergraduate or postgraduate level in tertiary institutes. Unfortunately, its price puts it into the public rather than the private library class.

S. J. MAINWARING

BOOK REVIEWS

Chemistry of the Environment
Bailey/Clark/Ferris/Krause/Strong
Harcourt Brace Jovanovich Group
Price: $36.35

"Chemistry of the Environment" is based on a course given by the authors to both undergraduate and postgraduate students at the Rensselaer Polytechnic Institute, Troy, New York. A basic knowledge of chemistry is assumed and the claimed intention of the authors is to bring the reader up to a level where he or she can understand the current literature in the environmental chemistry area. The book is not comprehensive in its coverage and it would be very difficult to be so at the level intended. Some topics are, therefore, covered in great detail and others not at all, the assumption being that it is the principles that are important and once these are understood thoroughly in one circumstance, they can readily be applied to a new and unfamiliar one. This is an educationally sound approach but it limits the text's value to teaching situations and those whose interests are specifically covered. It would, however, be a valuable addition to any library as the areas coverd in depth are, in the main, covered very well indeed.

If the book can be considered to have a theme then, it would have to be energy, the chemistry of its use, the chemistry of its products in the environment, and what the alternatives to conventional sources are, including more than 100 pages on nuclear chemistry. Other topics that are covered in depth are chlorinated hydrocarbons and pesticides, and the role of photochemistry in the atmosphere and the biosphere.

One minor criticism of the proof reading is that the degradation of a polystyrene cup featured in Figure 12.1 is actually occurring in the reverse order — a triumph over thermodynamics.

S. J. MAINWARING

ANNOUNCEMENTS

Unusual Promotional Opportunity

The sixth IUAPPA Congress will be held at the Palais de Congres, Porte Maillot, Paris 16-20 May, 1983. More than one thousand engineers, scientists, chemists, academics and others with great interest in clean air will attend.

There will be an exhibition of clean air equipment including cleaning, processing and extracting equipment; monitoring and analytical instruments and devices, conducted as an integral part of the Congress. The next opportunity of this kind for Australians to show their wares will not occur until 1986 at the Sydney Congress.

Like to know more? Contact the Secretariat of the Congress now! Telephone-Paris (1) 359 1030; Telex-Paris 640450 F Sepic; Write Sepic (APPA) 40 Rue du Colisee, F 75381, Paris, Cedex 08, France.

A PRELIMINARY STUDY OF AIR QUALITY IN BELL BAY, TASMANIA

LOW PAK SUM (BE,MEnvSt) and J.J. TODD (MSc,PhD)

Centre for Environmental Studies, University of Tasmania

SUMMARY

Some air quality and meteorological parameters for October, 1982 are presented for the Bell Bay area in the Tamar Valley, Tasmania. The area contains an aluminium smelter, a ferro alloys plant, and a 240 MW oil fired power station. The local wind regime is strongly influenced by the coastal valley environment with wind channelling along the valley as well as other effects such as the sea breezes, katabatic winds, temperature inversions, and fog and haze occurrence all being evident. Dust fallout measurements show that total dust, fluoride, and trace metals such as aluminium, manganese, zinc, and iron are all significantly higher within 2 to 3 km of the industrial area than in surrounding areas. Maximum observed fallout levels (expressed in $mg/m^2/day$) were: Aℓ, 1.8; Mn, 2.4; Fe, 2.8; Zn, 1.3; F, 2.0.

INTRODUCTION

The Tamar Valley lies on the northern coast of Tasmania. It stretches north-westerly from Launceston, the second largest city in Tasmania with a population of over 65 000, to West Head and Low Head on Bass Strait. The lower part of the eastern side of this valley embraces the Bell Bay industrial area where two large metal smelting industries (Comalco Aluminium (Bell Bay) Ltd and Tasmanian Electro Metallurgical Co. Pty Ltd (Temco)) and a number of smaller industries are located. A 240 MW thermal power station is located about 3 km south-east of the industrial area and a wood chip plant is a further 3 km south-east (Figure 1). The livelihood of George Town, which is about 4 km north-west of the industrial area, depends largely on the operation of the two heavy industries. It supports a population of about 7000. The towns of Beaconsfield and Ilfraville are on the opposite side of the valley. The Beaconsfield-Ilfraville area has a population of about 4000 and a large surrounding region of dairy farming lands and orchards.

The aluminium smelter was established at Bell Bay, in 1955. Its current production capacity is 117 000 tonnes of aluminium per year. Comalco Aluminium Powder Pty Ltd, which is located next to the smelter has been producing aluminium powder and paste since 1968. Temco, the only producer of manganese alloys, silicon alloys, and manganese sinter in Australia commenced operation in 1962. It produces approximately 135 000 tonnes of manganese alloys and 25 000 tonnes of silicon alloys annually. In addition, 240 000 tonnes of manganese sinter are produced each year. Comalco and Temco employ workforces of about 1300 and 450 respectively.

The oil-fired thermal power station was commissioned by the Hydro-Electric Commission (HEC) in 1971. It operates intermittently depending on water storage levels in the State's otherwise entirely hydro-electric power system. Fuel oil with a sulphur content ranging up to about 3 percent is burnt in the power station.

The two industries and the power station are subject to the provisions of the Tasmanian Environment Protection Act 1973 (as are other industries), although all three were established before this legislation was enacted. The air environment of Bell Bay and nearby areas has been of concern to many local residents, in particular the dairy farmers and orchardists. Some of this concern was expressed at a sitting of the Senate Select Committee on Air Pollution

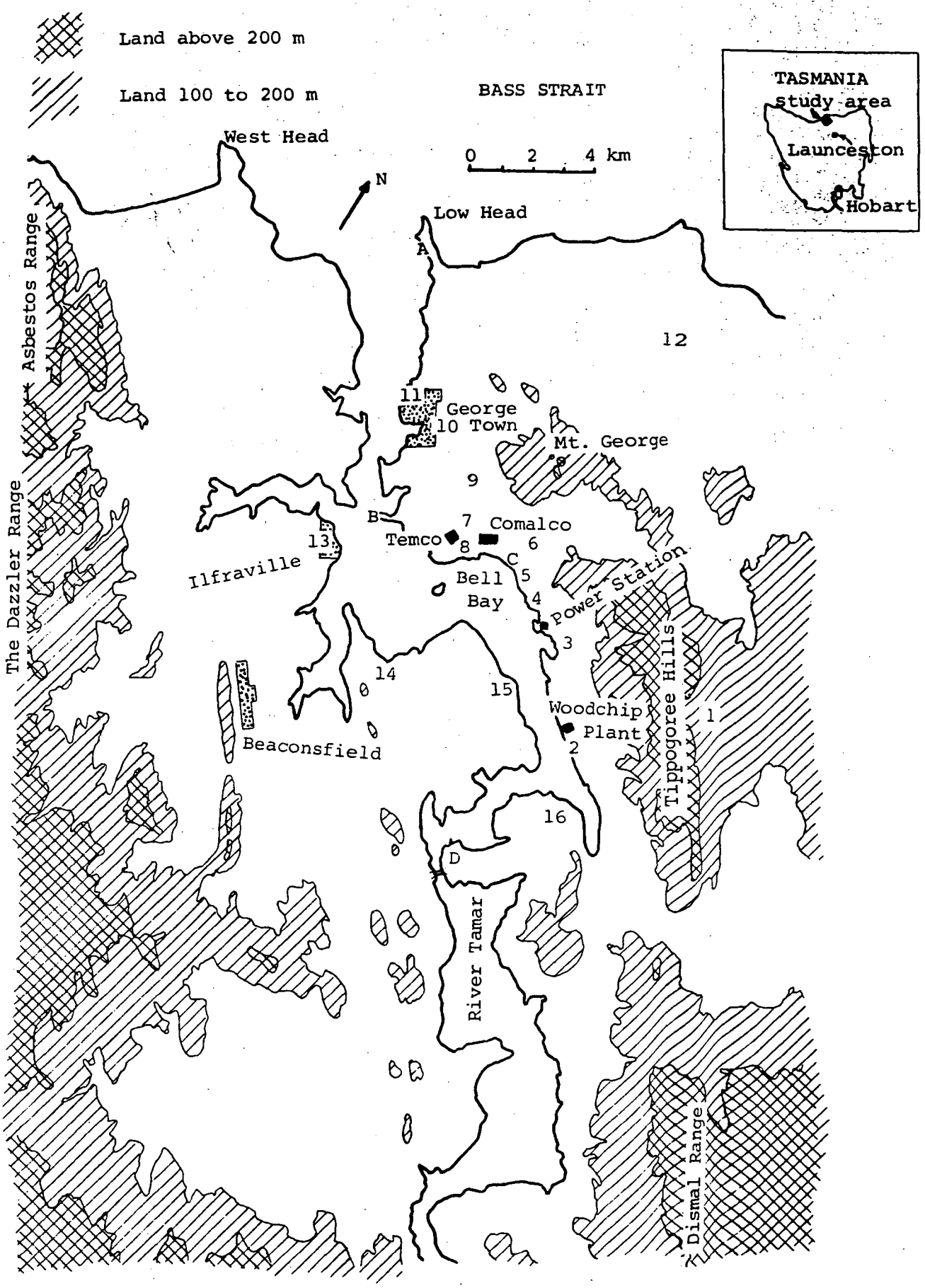


FIGURE 1. Lower Tamar Valley. The letters A to D mark the locations of the anemometer sites and the numbers 1 to 16 mark the locations of the dust fallout sites referred to in the text.

in George Town in 1969 (1). More recently, the 1979 proposal to convert the power station from oil to coal (2) prompted the formation of a local anti-pollution group (Tamar Valley Anti-Pollution Committee). Conversion plans were shelved but now preliminary investigations are underway in the State into the siting of a separate coal fired power station and the Tamar Valley is a possible choice.

In view of the almost two decades of concern about air quality in the area it is surprising how few meteorological and ambient air quality measurements have been made. Prior to this study only four dust fallout sites were monitored monthly (since 1972) by the Hydro-Electric Commission and the Tasmanian Department of the Environment, monthly fluoride fallout (in precipitation and vegetation) measurements were carried out by Comalco, and climatic conditions were recorded daily at the Low Head lighthouse by the Department of Transport.

Against this background, the present study was commenced in 1982 by the Centre for Environmental Studies at the University of Tasmania. This study aims to assess the air quality in the Bell Bay area and establish correlations between sources, ambient air quality, and various meteorological parameters. As is so often the case, the availability of equipment and funding constraints have meant that the programme has had to be fairly conservative in its specific objectives. Seven recording anemometers, a tethered balloon system, an extensive dust fallout array, high volume samplers, a dual tape fluoride sampler, and an air monitoring caravan (SO_2, NO_x, O_3, CO) have been used at various stages of the 16 month study. This paper presents some of the preliminary results for the month of October, 1982 which illustrate many of the more interesting aspects of the study.

METEOROLOGICAL STUDY

Many meteorological parameters affect the dispersion of air pollutants from a known source; wind speed and direction are among the most significant. The local topography and proximity to Bass Strait would be expected to have significant effects on the local wind regime. The Tamar Valley in the Bell Bay area is about 20 km wide bounded by hills 200 to 480 m high (Figure 2). The wind records available for the area were considered inadequate for the study so a network of recording anemometers was established.

Wind Data Analysis

Seven anemometers have been set up in the Tamar Valley between Low Head and Dilston (27 km SE of Bell Bay) since August, 1982. Only four had been established by October, 1982, their locations are shown in Figure 1. All four are Lambrecht Woelfle type which record wind run and direction on a waxed paper chart. All are set at a height above ground level of 10 m.

The wind frequency results for each site (Figure 3) for October show that NW winds are predominant during the month. Site A, which is nearest the coast experiences more westerlies than the other sites. Further into the valley surface wind directions are more influenced by the topography.

The NW winds, which could be reinforced by sea breezes, occurred most frequently in the afternoons (Table 1). Generally wind speeds were less the further the site from the coast (Table 2). For example, site D never experienced any strong breezes (i.e. wind speeds greater than 10.8 m/s), whereas, site A experienced these strong breezes much more frequently than site B or C. Table 2 also shows that calm (<0.5 m/s) or gale (>17.1 m/s) conditions were not experienced at any site. Fresh (8.0 - 10.7 m/s) to strong (10.8 -

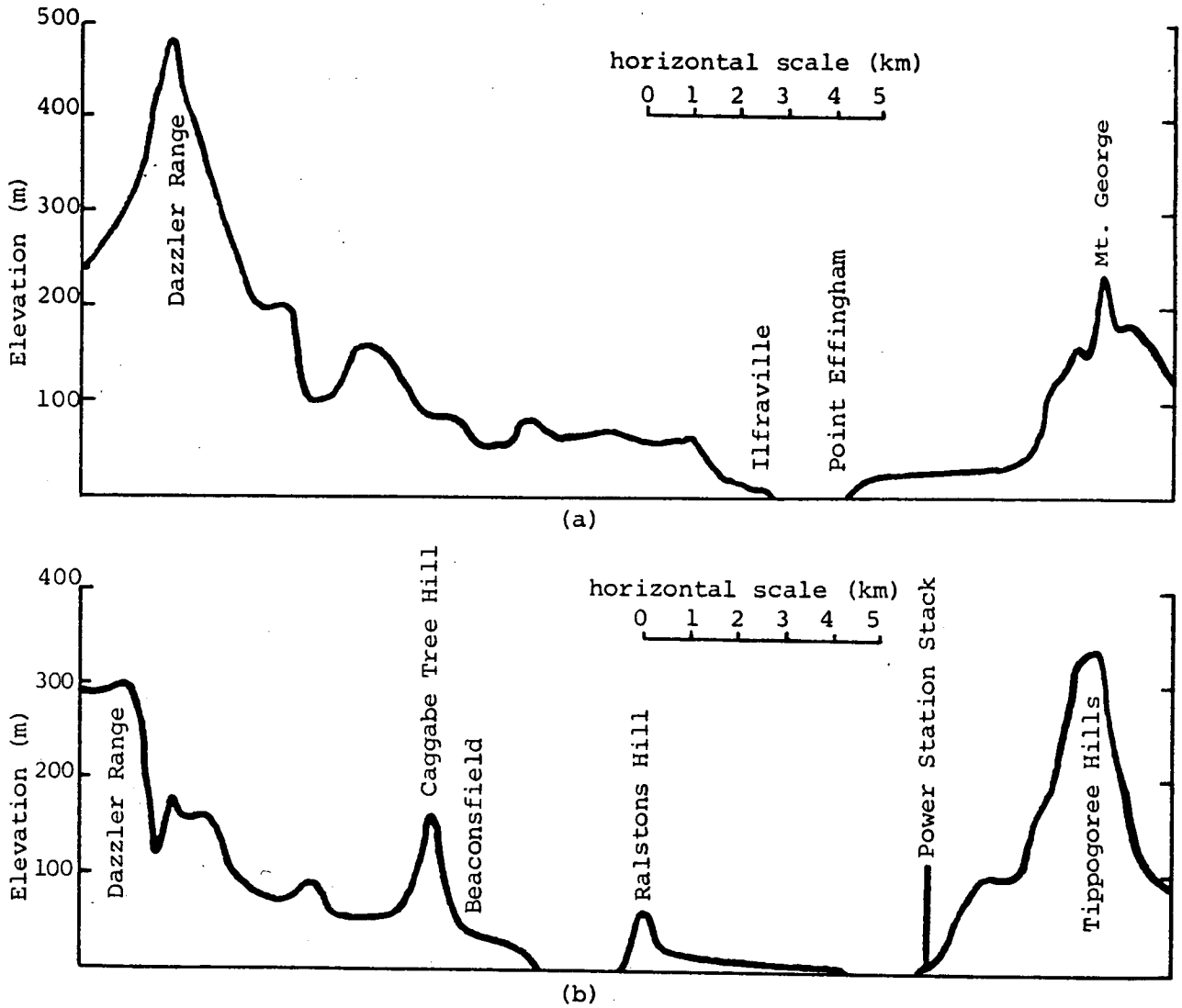


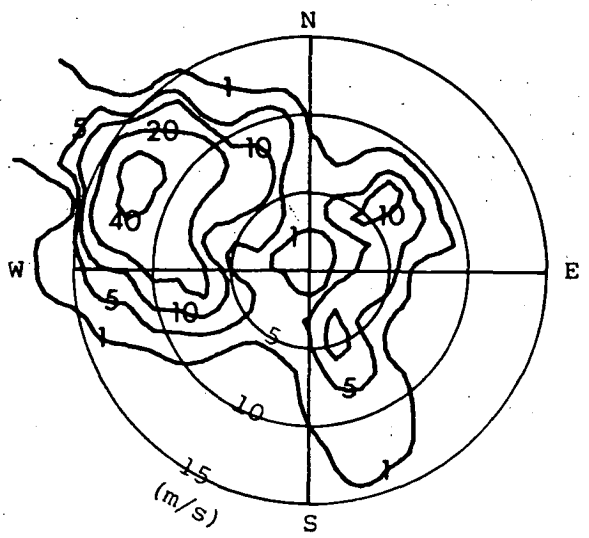
FIGURE 2. Lower Tamar Valley cross sections through (a) Mt. George/ Pt. Effingham and (b) the thermal power station/Beaconsfield.

13.8 m/s) breezes occurred more frequently in the afternoons, particularly at sites A and B, while light (1.6 - 3.3 m/s) to gentle (3.4 - 5.4 m/s) breezes occurred more frequently from late night to early morning, especially for sites B, C, and D.

S and SE winds were most frequent from about midnight to early morning indicating cold air drainage down the valley. Site C showed an interesting katabatic wind flow from the NE with a speed of 1.6 to 5.4 m/s caused by a small saddle between Mt. George and the Tippogoree Hills.

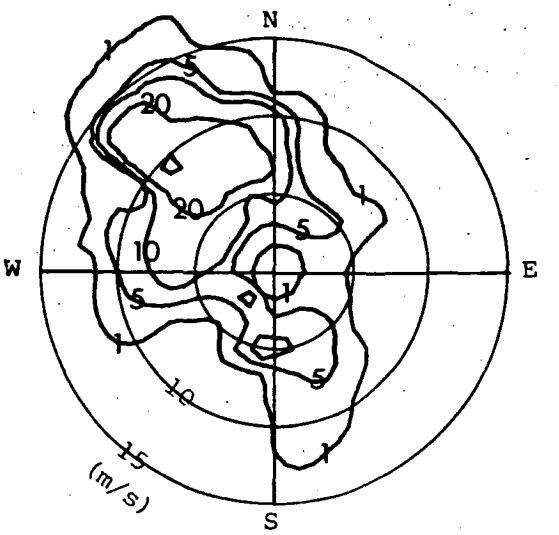
Sea Breeze

In the Tamar Valley, the sea breezes are likely to be important because they will disperse and dilute the air pollutants from the industrial area. However, they also carry any air pollutants further up the valley. Sea breeze conditions are illustrated by the wind speed and direction plots for 23 October shown in Figures 4 and 5. It appears that on this particular day the sea breeze began at about 10.00 a.m. at the coast (site A) and reached Point Effingham (site B) at about 11.30 a.m. and Batman Bridge (near site D) at about 12.45 p.m. The sea breeze front, moving slower than the wind speed itself, advanced inland at about 2.0 m/s which seems to be fairly typical (3).



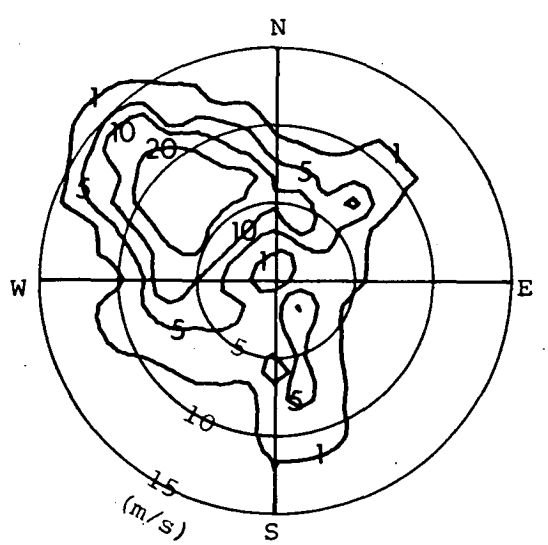
Site A

Number of observations	706
Variable winds	1
Calms	0



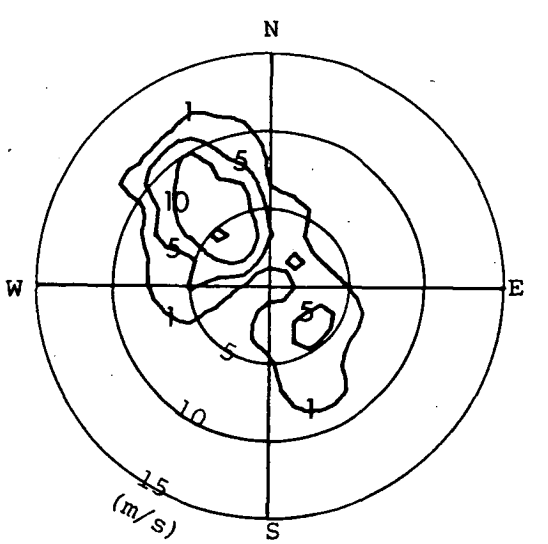
Site B

Number of observations	743
Variable winds	28
Calms	0



Site C

Number of observations	671
Variable winds	36
Calms	0



Site D

Number of observations	406
Variable winds	26
Calms	0

FIGURE 3. Monthly Wind Roses for All Hours - October, 1982. Contours show frequency of occurrence at various speeds and directions. The frequency levels drawn are 1, 5, 10, 20, and 40. The concentric circles represent wind speeds of 5, 10, and 15 m/s.

TABLE 1

Percentage of occurrence of wind direction (8 compass-points) at various hours of the day for October, 1982 at the four wind stations (A, B, C, and D, see Figure 1) in the Lower Tamar Valley.

Site \ Time (hrs)	0300				0600				0900				1200				1500				1800				2100				2400			
Direction	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
Calm	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NE	3	6	11	0	3	0	14	0	14	3	7	7	14	0	14	0	13	3	4	8	17	13	4	7	10	19	7	21	3	6	11	0
E	0	6	7	7	0	0	4	0	3	0	0	0	0	0	0	7	0	0	4	0	3	0	0	0	10	0	0	7	7	6	4	7
SE	28	0	11	21	10	6	7	29	10	13	0	21	0	3	0	21	0	0	0	8	0	0	11	0	7	3	7	0	27	3	7	7
S	14	19	7	21	24	23	14	21	7	16	14	14	7	7	11	0	0	3	7	0	0	0	4	0	7	6	14	0	7	3	7	7
SW	3	10	7	0	3	3	0	0	3	0	11	0	0	0	4	0	0	0	4	0	0	0	4	0	7	0	0	7	10	23	7	14
W	31	10	14	7	38	13	11	0	34	19	14	0	10	17	14	14	20	16	11	8	30	16	14	13	37	26	29	7	27	3	19	7
NW	17	29	25	29	14	39	39	29	21	26	29	36	55	43	36	57	57	45	43	54	47	48	46	47	23	29	25	29	20	42	22	29
N	3	16	14	14	3	10	7	14	7	23	21	14	14	30	14	0	10	29	18	23	3	23	14	33	0	6	14	14	0	3	15	0
Variable	0	3	4	0	3	6	4	7	0	0	4	7	0	0	7	0	0	3	11	0	0	0	4	0	0	10	4	14	0	10	7	29
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

TABLE 2

Percentage of occurrence of wind speed at various hours of the day for October, 1982 at the four wind stations (A, B, C, and D, see Figure 1) in the Lower Tamar Valley.

Time (hrs) / Site	0300				0600				0900				1200				1500				1800				2100				2400			
Wind Speed (m/s)	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
<0.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0.5-1.5	0	0	7	29	0	0	7	7	0	0	0	14	0	0	4	0	0	0	4	0	0	0	11	7	3	10	14	29	0	3	11	43
1.6-3.3	21	29	21	36	14	23	21	36	7	16	7	7	0	7	7	29	3	3	18	15	7	13	11	27	23	23	25	50	23	45	19	43
3.4-5.4	17	42	36	21	24	39	32	50	21	23	36	43	28	20	11	14	13	13	11	31	27	29	21	53	17	23	25	14	27	19	48	14
5.5-7.9	31	10	18	14	24	23	25	7	21	23	32	29	14	23	46	29	30	26	25	38	7	19	36	7	27	35	36	7	23	23	19	0
8.0-10.7	17	13	11	0	21	13	7	0	31	32	25	7	31	27	18	29	23	32	32	15	33	29	21	7	17	10	0	0	23	10	4	0
10.8-13.8	10	6	7	0	17	3	7	0	21	6	0	0	28	23	14	0	27	19	7	0	23	10	0	0	13	0	0	0	3	0	0	0
13.9-17.1	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	6	4	0	3	0	0	0	0	0	0	0	0	0	0	0
>17.1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

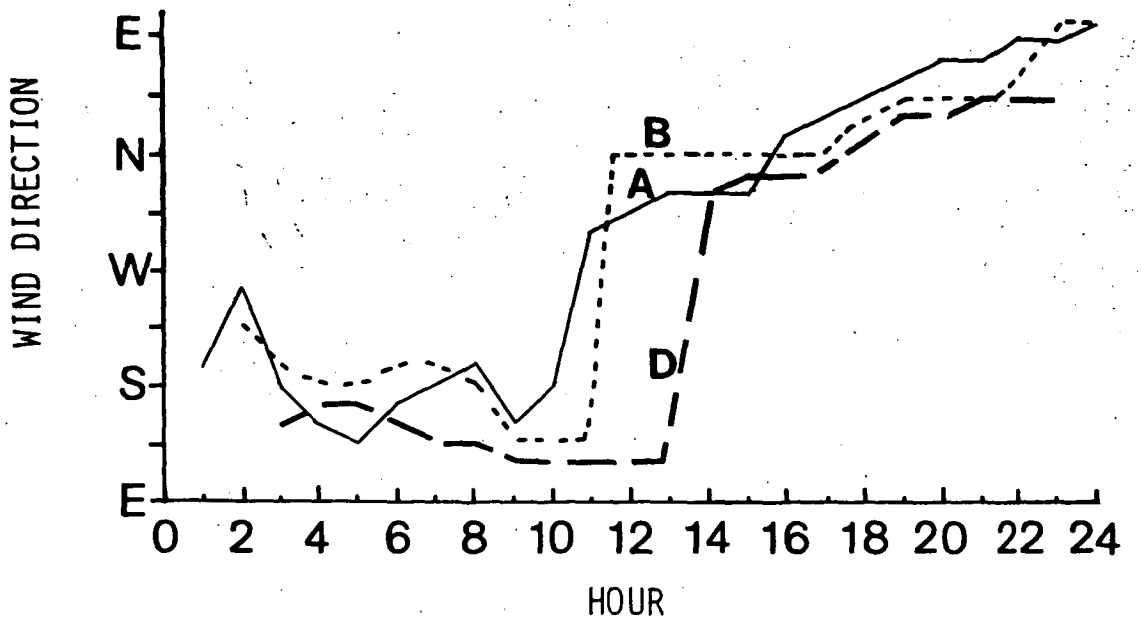


FIGURE 4. Wind direction as a function of time on 23 October, 1982 at sites A, B, and D. The sea breeze began at about 10 a.m. at the coast, and reached Point Effingham (site B) and Batman Bridge (near site D) at about 11.30 a.m., and 12.45 p.m., respectively.

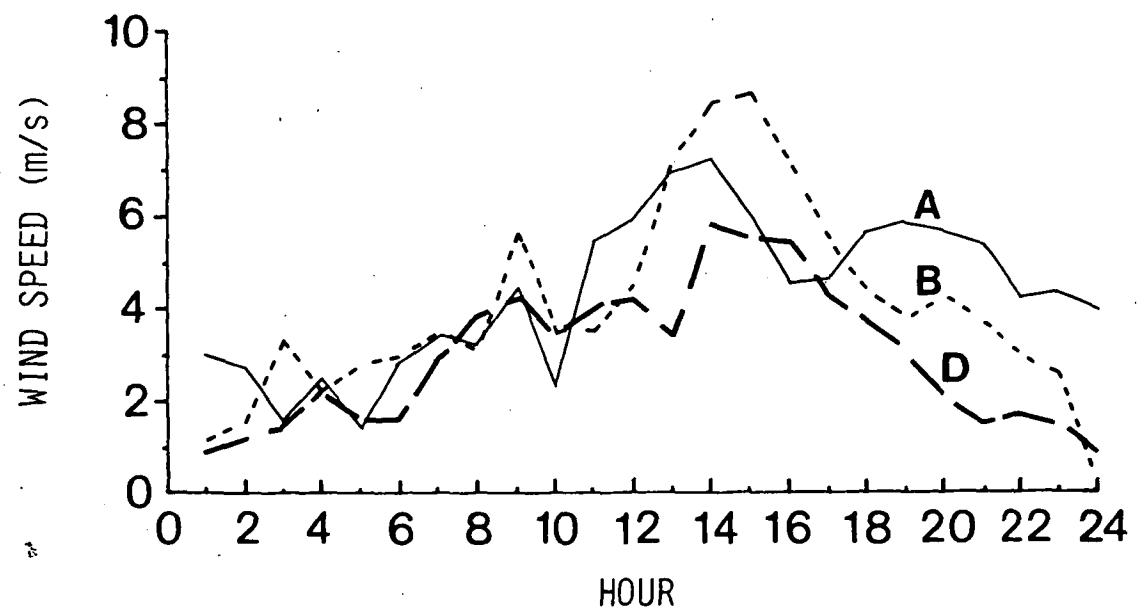


FIGURE 5. Mean hourly wind speed as a function of time on 23 October, 1982 at sites A, B, and D.

The wind speed increased during the sea breeze period. Wind speeds at site B were higher than at site A during this period. This could be caused by the funnelling effect as the breeze enters the valley.

Tethersonde System

It has been pointed out that the airflow well above a coastal valley is sometimes markedly different from that near the ground and neither flow is easily predicted from the gradient wind for the region (4). A tethersonde system was, therefore, used on several occasions to gain some appreciation of the planetary boundary layer conditions. A high pressure system centred over Tasmania often led to the calm cloudless night conditions suitable for using the tethersonde and for detecting inversions and the structure of the katabatic and gradient winds.

The equipment available was a tethered boundary layer profiling (BLP) system model TS-1A tethersonde and TS-2AR ground station manufactured by Atmospheric Instrumentation Research Inc. Five balloon flights were possible in October from a location near anemometer site C (Figure 1).

Temperature and Wind Profile

The temperature and wind profiles for an early evening flight on 5 October are shown in Figure 6. The temperature profile shows that during this particular flight, surface temperature inversion developed up to a height of about 30 m and the elevated temperature inversion occurred at a height of about 425 m. Obviously, these inversions are very important in terms of pollution dispersion. In this case the base of the elevated inversion is below the height of some of the hills on the western side of the valley (Figure 2). The temperature profile also shows an isothermal layer from about 280 to 380 m. The actual lapse rate of the mixing layer (in this case from about 50 to 220 m) is 9.6^{o}C/km, which is close to the dry adiabatic lapse rate for unsaturated air (9.8^{o}C/km) and means the layer is classified as a neutral atmosphere. The actual lapse rate in the upper inversion layer is about -12^{o}C/km, above the inversion layer the lapse rate is about 5^{o}C/km. The ground level inversion is probably caused by radiation cooling just after sunset but it is likely that there is some influence of low level (20 to 50 m) heating of the atmosphere from thermal emissions from the aluminium smelter (a localised heat island has been observed in ground level temperature mapping).

The wind speed decreases above the base of the upper inversion layer. At a height of about 500 m (just above the western hills) the wind comes from a more westerly direction. This suggests a different wind regime above the valley.

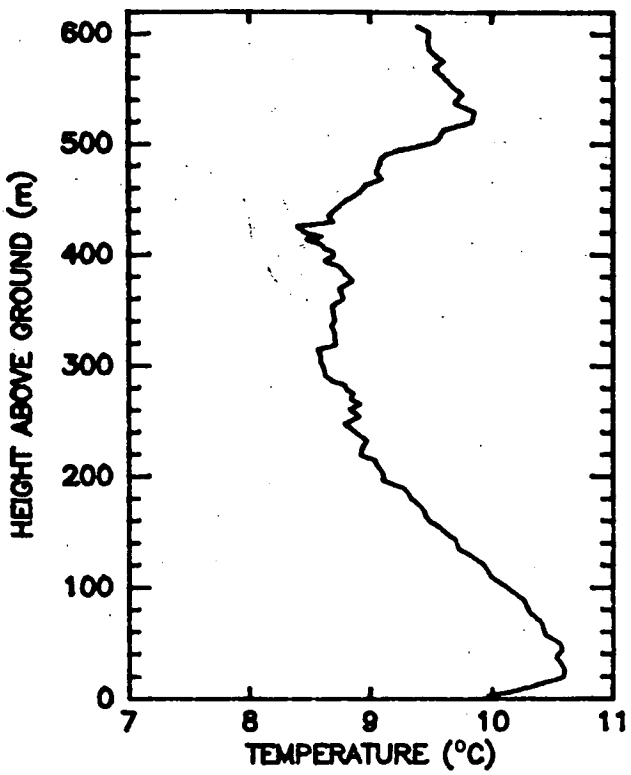
Other Meteorological Observations

The Bell Bay Port Office has co-operated by recording four hourly observations of fog and haze occurrence. In October fog occurred once and haze occurred twice (in both cases the haze began in the late afternoon). Two thermohygrographs were also used to give daily temperature and humidity data at Pt. Effingham and Mt. George.

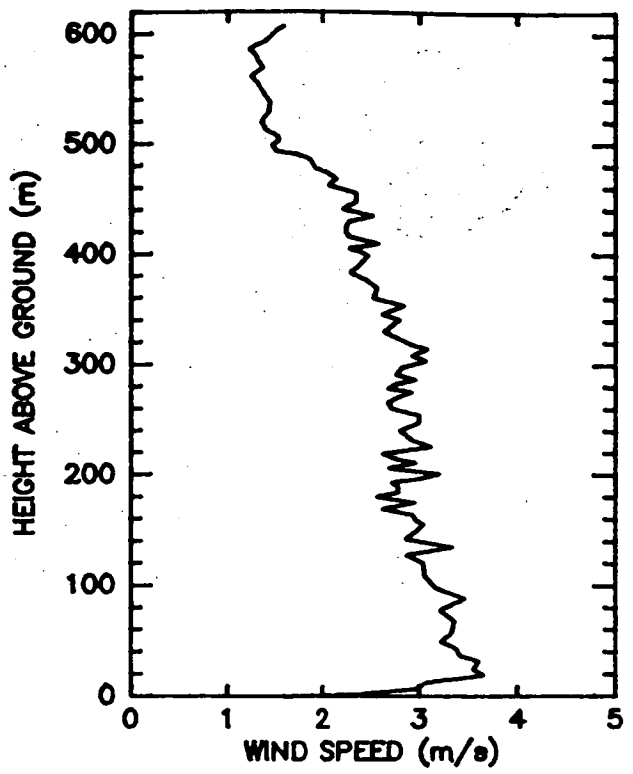
AMBIENT AIR MONITORING

Sample Collection and Analysis

In order to adequately cover the survey area, 16 dust fallout gauges were added in July, 1982 to the existing dust monitoring network (5). The



(a)



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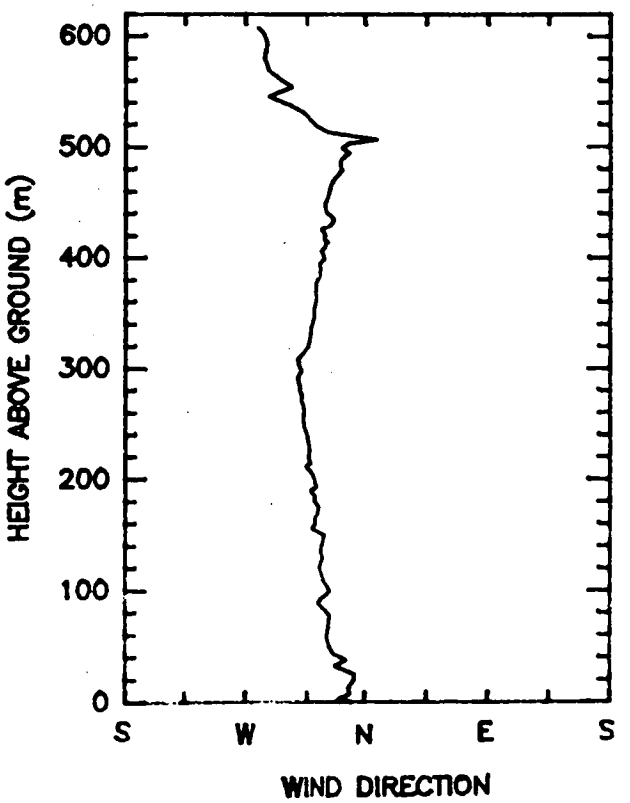

(c)

FIGURE 6. The vertical temperature (a), wind speed (b) and wind direction (c) profiles measured by the tethersonde at Bell Bay from 1820 to 1855 hours Eastern Standard Time on 5 October, 1982. Ground level is about 40 m above sea level.

dustfall sampling locations are shown in Figure 1. Each dust fallout gauge consists of a conical glass funnel with a nominal diameter of 145-150 mm fitting into a 4.5 litre glass bottle with a rubber stopper. These gauges are being used by the Department of the Environment in Tasmania. Similar gauges are also widely used in other states of Australia (6).

The dust fallout gauges are all placed on wooden stands. The height of each gauge above the ground is about 3 m (as measured from the top of the funnel). This is more than double the minimum height for the British Standard Dust Deposit Gauge (1.2 m) (7) and also well above the minimum height (2.4 m) recommended by the U.S. Air Pollution Measurement Committee (8). The 3 m height effectively minimises the deposition of dust from the ground near the gauge.

The dust fallout samples are collected at the end of each month. Soon after collection the pH is measured using a Pye Unicam Model 290 MK2 pH meter, then each sample is filtered through a washed preweighed cellulose acetate membrane filter of 0.45 µm porosity. The volume of the filtrate is measured, then 20 ml is buffered with the same volume of a total ionic strength adjustment buffer (TISAB) for subsequent determination of fluoride using a Philips PW 9414 digital ion-activity meter. The buffer was prepared in accordance with the American Standard Method (9). About 60 ml of the filtrate is acidified and used for analysis of dissolved trace metals using atomic absorption spectrophotometry (AAS). After determining the dried weight, the insoluble dust or residue collected on the filter is digested in boiling concentrated nitric acid for determination of trace metals which include Aℓ, Mn, Zn, Fe, Cu, Cd, Co, Pb, Ni, and Cr by AAS. The analytical method for dust fallout is the same as that described by Ayling and Bloom (10).

Dust Fallout

The total water insoluble dust and the most significant trace metals (Aℓ, Mn, Fe, Zn) deposited in the various sampling locations during October are shown in Table 3. The other trace metals showed fallout levels (in $\mu g/m^2/day$) of: Cu (0.5 to 11.3), Cd (0 to 3.0), Co (0 to 5.3), Pb (0.8 to 84.0) Ni (1.1 to 15.1), and Cr (0 to 2.6).

Total insoluble dust levels ranged from 17 to 163 $mg/m^2/day$. The significance of these values in absolute terms is difficult to assess because the dustfall in a particular area is very much a reflection of the climatic conditions, topography, and the survey and analytical techniques in addition to the emissions from individual sources. However, the results do show that most sites within about 2 to 3 km of the industrial area have much higher fallout levels. One exception is location 12 which is intended to give an indication of background levels. In this case the high reading was caused entirely by bird droppings, a common problem but easily detected by inspection of the sample. The relatively low levels of trace metals in the dust at location 12 support this non-industrial explanation and it illustrates the importance of including trace metal analysis for use as an indicator of the source of the fallout.

Table 3 shows that sites close to the industrial area (locations 5, 7, and 8) all have significantly higher levels of Aℓ, Mn, Fe, and Zn fallout than sites further away. Some of the more interesting features of the fallout measurements include:

- The initial rapid and then more gradual decrease in Al fallout (along the NW and SE directions) and Mn fallout (along the NW direction) with distance from the industrial area as illustrated in Figure 7.
- The relatively high levels of total dust and trace metals in Ilfraville (location 13). This is probably caused by the localized cold air drainage from the NE.

TABLE 3

Dust fallout measurements, George Town Area.
Average daily fallout of total dust, various trace metals and pH of collected rainfall for the month of October, 1982.

Site[a]	Total Dust (mg/m^2/day)	Trace Metals in Fallout (µg/m^2/day)								F (ppm)	pH
		Aℓ[b]	Fe[b]	Zn			Mn				
				Sol.	Insol.	Total	Sol.	Insol.	Total		
1	17	221	174	7	5	12	10	24	44	0.11	5.5
2	28	500	563	12	8	20	102	100	202	0.38	5.8
3	16	666	402	118	14	132	131	160	291	0.36	5.9
4	25	830	574	131	12	143	207	201	408	0.83	5.7
5	118	1688	2812	6	36	42	16	300	316	1.60	8.0[d]
6	8	563	298	15	5	20	110	77	187	0.43	5.7
7	153	1235	1369	399	444	843	409	1744	2153	0.25	6.1[d]
8	163	1816	1787	-[c]	97	97	55	2387	2442	0.79	8.2[d]
9	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
10	68	1007	921	21	251	272	125	513	638	0.11	6.1
11	62	796	1691	391	49	440	38	426	464	0.09	6.6
12	129	238	338	12	23	35	11	16	27	0.04	8.7[d]
13	86	778	1791	326	976	1302	25	231	256	0.10	6.1
14	28	404	631	-[c]	15	15	16	27	43	0.06	6.2
15	19	610	445	-[c]	11	11	232	361	593	0.18	6.7
16	18	340	324	21	12	33	49	61	110	0.25	5.6

NOTES

(a) The site numbers refer to the dust fallout collection locations shown on Figure 1.
(b) Only insoluble (non-filterable) Aℓ and Fe were measured.
(c) Concentration was below detection limit of the analysis.
(d) These samples were contaminated with algae which could affect the pH. Total dust could be increased but observations of the samples suggested the effect would be minimal (i.e. very little algae). Some trace metals could have been retained in algae which was not washed out of the sampling bottle but this is expected to be minimal because of careful washing.

n.a. not available because sample was damaged.

- The low dust levels measured at location 6 which is only about 1 km NE of the industrial area. The concentration (µg of metal per mg of dust) of Aℓ and Mn in the dust at this location is quite high suggesting an industrial source, but the low total levels reflect the infrequency of SW winds.
- The higher than background levels of Al and Mn at location 16, about 10 km SE of the industrial area, suggest transport of dust at least that far by the predominant NW winds. Analysis of data for other months should give a more precise estimate of the extent of dust transport.

Fluoride Fallout

Fluoride compounds (both gaseous and particulate) are the major air pollutants emitted by the aluminium smelter industry. The gaseous fluoride emissions include hydrogen fluoride (HF), which is highly reactive and corrosive, silicon tetrafluoride (SiF_4), carbon tetrafluoride (CF_4), hexafluoroethane (C_2F_6) and the particulate fluoride emissions include cryolite (Na_3AlF_6), aluminium fluoride (AlF_3), calcium fluoride (CaF_2) and chiolite ($Na_5Al_3F_{14}$) (11).

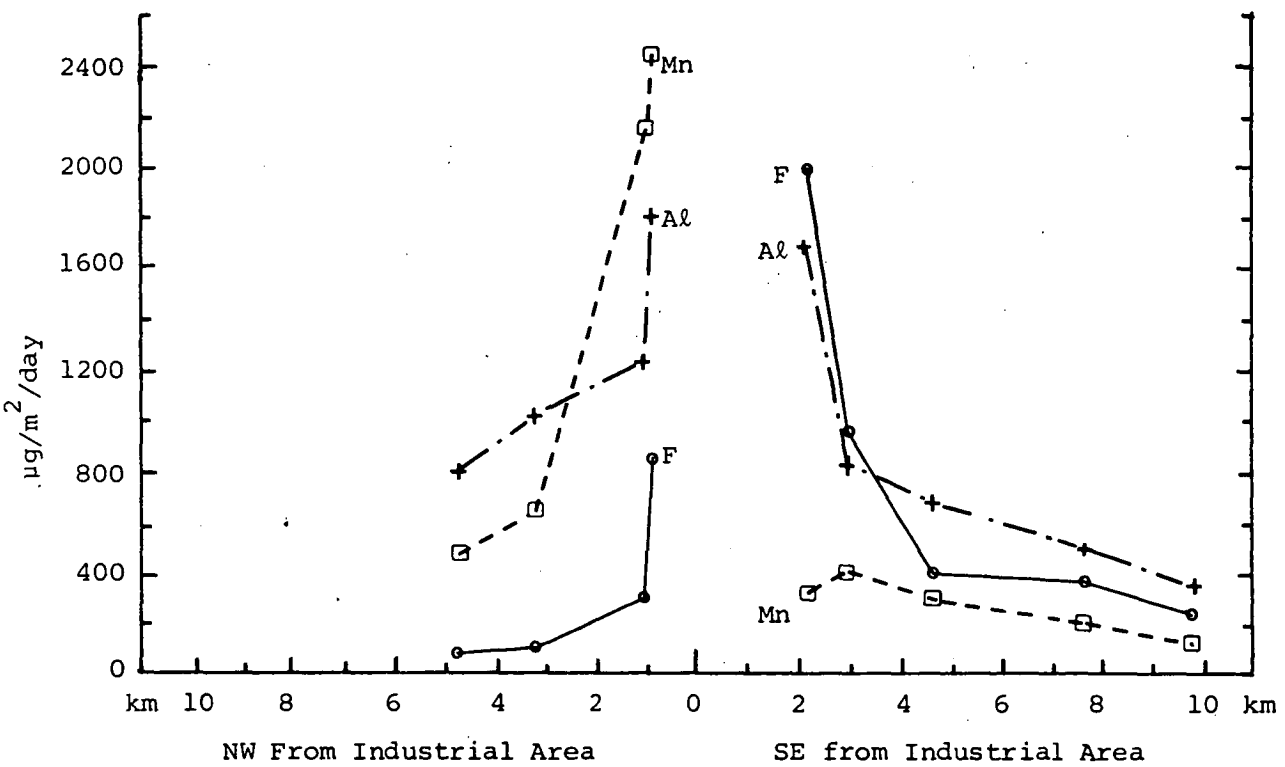

FIGURE 7. A Plot of Aℓ, Mn, and fluoride fallout as a function of distance from the Bell Bay Industrial Area. In general these fallout levels decrease with distance from the area. The points on the graph (from the left) refer to sampling locations 11, 10, 7, 8 (NW of industrial area), 5, 4, 3, 2, and 16 (SE of industrial area) (see Figure 1).

Fluoride compounds are acute toxicants to vegetation and vegetation damage can be used as an indicator of fluoride pollution. Once emitted into the atmosphere, the fluoride compounds enter into a complex biogeochemical cycle, the pathways of which are only partially understood (12).

The fluoride measurements for October (Table 3) show that the concentration in the fallout ranges from 0.04 ppm (background) (13) to 1.6 ppm (1.5 km from the aluminium smelter). If these concentrations are expressed in

terms of total fallout (i.e. concentration multiplied by rainfall collected) then the range is 51 to 1995 $\mu g/m^2/day$. The spatial distribution of fluoride fallout is similar to that for the trace metals (Figure 7). In short, the fluoride fallout pattern seems to be strongly influenced by the predominant NW winds coupled with SE winds and localized cold air drainage from NE of the smelter.

Some error in fluoride measurements could occur because of the use of glass bottles and funnels. Comparative measurements were subsequently made which indicated glass containers gave generally lower fluoride measurements than plastic containers particularly at low fluoride levels. Detailed analyses of these measurements are continuing.

pH Measurement

Much has been said about acid rain in Europe and North America in recent years. Precipitation is usually considered acidic if the pH is less than 5.6, the pH of "normal, unpolluted rain" (14). However, Sequeira (15) argues that a pH of 5.6 is not a logical reference value because pH can also be strongly influenced by alkali materials. He points out that in unpolluted maritime environments the mean pH of precipitation (based on monthly collection) can range from 4.9 (Hawaii) to 6.1 (Cape Grim, Tasmania).

The dust fallout samples collected in this study included both dry and wet depositions of air pollutants from the atmosphere. The measurement of pH of these samples will give some indication of the relative acidity at various locations. The pH of the dust fallout samples for October ranged from 5.5 to 6.6 (excluding those samples which were contaminated by algae and bird droppings). It is not possible to draw any conclusions from these figures at this stage.

After the discovery of some low pH samples in other months (the lowest value recorded was 4.2), further steps have been taken to analyse the chemical composition of the samples. Immediate rain samples have also been collected for analysis. These results are not yet available. The thermal power station was not in operation in October, 1982.

DISCUSSION

It is difficult to draw any conclusions on the correlation of air quality and local meteorology with only one month's data analysed from the 16 month programme. These preliminary results show that the total dust, trace metals and fluoride fallout levels are significantly higher within 2 to 3 km of the Bell Bay industrial area and that the fallout distribution pattern is strongly influenced by the local wind patterns. The analysis of the meteorological data shows that NW winds are predominant, particularly in the afternoons, while S to SE winds are more frequent from about midnight to early morning. The prevailing winds from the NW and SE directions are clearly related to the physical orientation of the valley. Other local meteorological effects evident are sea breezes, cold air drainage, fog and haze occurrence, wind funnelling within the valley, and temperature inversions capping the valley.

The micro-meteorology in the study area is quite complex because of the local topography. It will require the collection and analysis of more data before it is possible to mathematically model the transport of emissions from the major industries realistically and compare the predicted air quality parameters with those actually observed.

The monthly average fallout is difficult to correlate with the meteorological conditions because of the many parameters which can change over the month. The regular suspended particulates (high volume) sampling programme

which commenced in March, 1983 should allow more direct comparison of emission dispersion with local meteorological conditions because of the shorter collection period (normally 24 hours). Two types of high volume filters, namely Whatman GF/A glass microfilters and Schleicher & Schüll membrane filters (0.2 μm porosity) have been used. The former is conventionally used by the Tasmanian Department of the Environment for its regular suspended particulates monitoring work. The latter, which is more expensive, has the advantage of containing no traces of metals and hence provides an easier identification of the sources of air pollution. The high volume samples collected with these filters are being studied using Fourier Transform Infra Red (FTIR) spectroscopy, electron probe microanalysis, and atomic absorption spectrophotometry. This, hopefully, will allow some knowledge on chemical speciation of the major emissions to be gained.

Results from the air monitoring caravan (O_3, SO_2, CO, and NO_x) and the dual tape fluoride sampler are not yet available but they would help to provide a better picture of the air quality in the study area.

ACKNOWLEDGEMENTS

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SURFACE WIND STATISTICS FOR THE TAMAR VALLEY, TASMANIA

LOW PAK SUM

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ATMOSPHERIC DEPOSITION IN THE LOWER TAMAR VALLEY, TASMANIA

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SUMMARY

AS PART OF AN AIR QUALITY STUDY IN 1982-83, ATMOSPHERIC DEPOSITION WAS MONITORED IN THE LOWER TAMAR VALLEY WHERE AN ALUMINIUM SMELTER, A FERRO ALLOYS PLANT, AND AN OIL-FIRED THERMAL POWER STATION ARE LOCATED. THIS PAPER PRESENTS THE RESULTS FROM SEPTEMBER 1982 TO AUGUST 1983. THE MEAN DEPOSITION RATES OF DUST AND THE MAJOR CHEMICAL CONSTITUENTS (Al, F, Mn AND Fe) IN RELATION TO THE METEOROLOGICAL PARAMETERS, IN PARTICULAR THE WIND VECTORS, FOR THE PERIOD ARE DISCUSSED. THE VARIOUS TRACE ELEMENTS ARE STATISTICALLY CORRELATED, HENCE THEIR SOURCES IDENTIFIED. THE ACIDITY OF THE DEPOSITION SAMPLES IS INVESTIGATED. PRELIMINARY RESULTS ON CHEMICAL SPECIATION OF PRECIPITATION SAMPLES USING FOURIER TRANSFORM INFRARED (FT-IR) SPECTROSCOPY ARE PRESENTED.

INTRODUCTION

Bell Bay industrial area, located on the eastern shore of the lower Tamar Valley, about 50 km NW of Launceston (second largest city in Tasmania with a population of about 65,000) and 4 km SE of George Town (population 7,300), is one of the most important industrial centres in northern Tasmania. The area, bounded by Asbestos/Dazzler Ranges and various other low hills in the west, and Mt. George/Tippogoree Hills in the east, contains two metal smelting industries, namely Comalco Aluminium (Bell Bay) Ltd., and Tasmanian Electro Metallurgical Co. Pty. Ltd. (Temco), which were established in 1955 and 1962 respectively, and a few other smaller industries including a Pioneer concrete mixing plant, Mobil and BP oil storage depots. A 2 x 120 MW oil-fired thermal power station, established in 1971, is located about 3 km SE of the industrial area. Two woodchip plants are a further 3 km SE at Long Reach. The good all-weather port at Bell Bay is equipped to handle all types of vessels and cargo (Figure 1).

Of the various sources of air emissions in the lower Tamar Valley, the two heavy industries and the thermal power station, all of which were established before the enactment of the Tasmanian Environment Protection Act 1973, are the major ones. The main air emissions from these three sources include the gaseous and particulate F compounds (notably from Comalco), Mn, Fe and Si compounds particulates (notably from Temco), gases such as SO_2, SO_3, NO_x, CO and CO_2 (particularly from the power station), fugitive dust, fly ash and hydrocarbons. The adverse effects of these air emissions on the physical and human environment are well documented in literature, though their synergistic effects have yet to be fully assessed. The air environment of the lower Tamar Valley has been of concern to the local residents, particularly the dairy farmers and orchardists, ever since the development of the Bell Bay industrial area began. This concern has grown over the years, and precipitated over the proposed conversion of the power station to coal-firing in 1979 (1). Against this background, an air quality study in the lower Tamar Valley was undertaken. The major parts of this study, which included intensive and extensive meteorological and ambient air monitoring programmes, began in July 1982 and ended in August 1983.

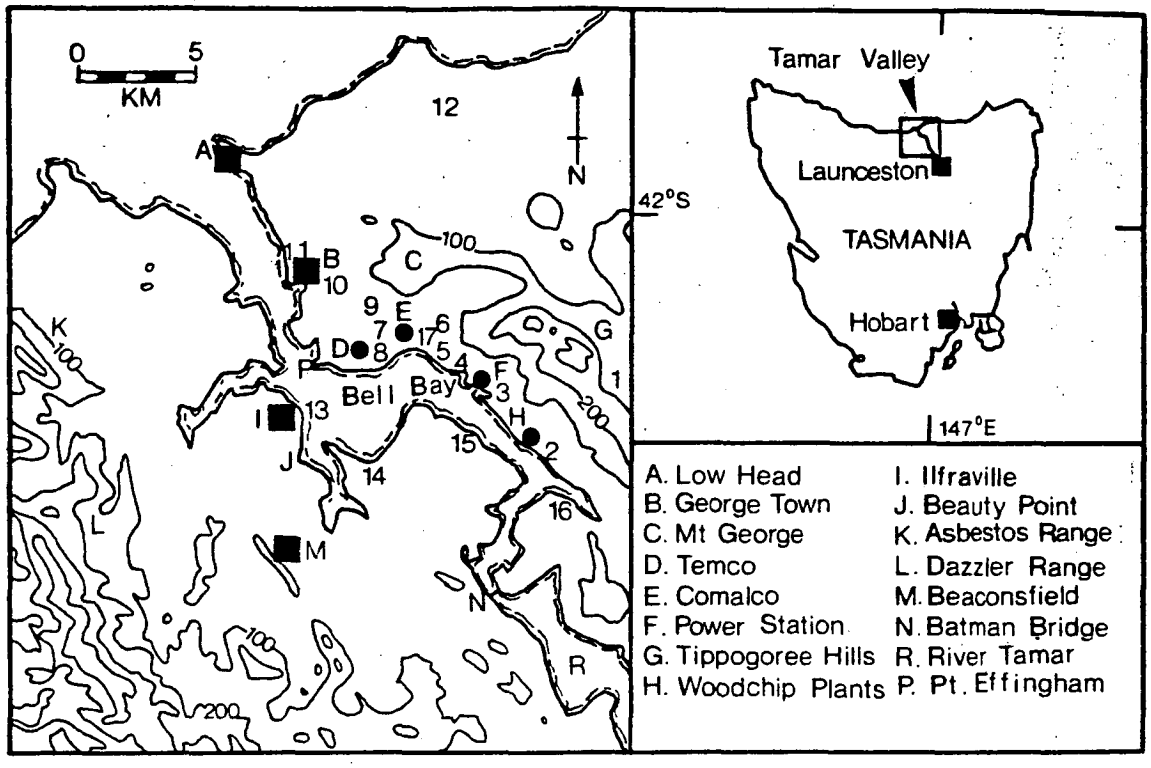

Figure 1. Lower Tamar Valley showing locations of deposit gauges (1-17).

This paper discusses the results of atmospheric deposition monitored from September 1982 to August 1983.

MONITORING NETWORK

The atmospheric deposition samples were collected in glass deposit gauges at 17 carefully chosen locations along the lower Tamar Valley (Figure 1). The details of the monitoring network are given in Low and Todd (1). Location 12 was intended for 'background' deposition as it was behind Mt. George (242 m high), about 8 km NNE from Comalco on a remote dairy farm. Wind records provided by the Bureau of Meteorology show that this location was more likely to be influenced by the westerlies than the NW and SE winds which are predominant along the Tamar Valley. This is confirmed by the wind data obtained during the study period (2). However, a strong SSW wind could bring air emissions from the industrial area to this location. Thus this intended 'background' location should be regarded as 'relative' rather than 'absolute'. The limitations of deposit gauge as a collection device have been well discussed by Noller, Bloom and Arnold (3).

CHEMICAL ANALYSES

The bulk (wet and dry) deposition samples were collected monthly. Soon after collection the pH of each sample was determined. This was followed by a series of chemical analyses on the soluble and insoluble portions of the samples. The concentration of soluble fluoride was determined using a Philips PW 9414 digital ion-activity meter (1). Soluble and insoluble trace metals (Al, Mn, Fe, Zn, Cu, Cd, Co, Ni, Cr and Pb) were analysed by flame atomic absorption spectrometry (AAS) (4). Chemical speciation of the soluble components of some selected samples was examined using a Digilab FTS-20E Fourier transform infrared spectrometer.

RESULTS AND DISCUSSIION

Deposition Rates of Dust, Al, F, Mn and Fe

While Comalco maintained full annual production capacity (117,000 tonnes Al) in 1982-83, Temco greatly reduced production (from a full annual capacity of 135,000 tonnes FeMn, 25,000 tonnes SiMn, and 220,000 FeMn sinter to 73,135 tonnes FeMn, 7,530 tonnes SiMn, and 95,073 tonnes FeMn sinter) in the same period due to world economic recession. Hence the results presented below should be viewed in this perspective.

Only the mean deposition rates (or fluxes) of the insoluble dust (mg/m^2/day) and the trace elements Al, F, Mn and Fe ($\mu g/m^2$/day) at each sampling location for the period are discussed. The concentrations of soluble Al and Fe are insignificant compared with those of soluble Mn, while insoluble F was not measured. These four elements, though commonly found in soils and sea-sprays, are used as elemental tracers of the air emissions from Comalco (Al and F) and Temco (Mn and Fe). By comparing the deposition rates of these elements at various locations with that of the intended 'background' location, it is possible to identify their sources of emissions.

The mean deposition rates of dust ranged from 32.4 to 338.3 mg/m^2/day. The sampling locations within 2 km of either Comalco or Temco (locations 5,7,8,9 and 17) had mean deposition rates higher than 80 mg/m^2/day. Although various yardsticks have been proposed for 'acceptable' dustfall levels in residential, rural, light and heavy industrial areas both overseas and in Australia (5,6), it must be stressed that for dustfall levels at different places and countries to be comparable, similar dust collectors as well as sampling and analytical methods must be employed, preferably for similar settings or topography, emission sources, and meteorological conditions.

The mean deposition rates of Al, F, Mn(total) and Fe ranged from 445 to 5,640, 89 to 12,570, 38 to 3,675, and 392 to 1,535 $\mu g/m^2$/day respectively. Normalising the mean deposition rates to the intended 'background' levels (which were the lowest in all cases), the ratios vary from 1.2 to 12.7 for Al, 1.7 to 139.8 for F, 1.8 to 97.8 for Mn(total), 1.5 to 4.0 for Fe. While location 17, about 1 km ESE of Comalco, had the highest mean deposition rates of Al (5,640 $\mu g/m^2$/day) and F (12,570 $\mu g/m^2$/day), location 8, about 1 km E of Temco, recorded the highest mean deposition rates of total Mn (3,675 $\mu g/m^2$/day) and Fe (1,535 $\mu g/m^2$/day). In general, the mean deposition rates of the trace elements were much higher within 3 km of their respective emission sources, though the air emissions from Comalco and Temco could travel at least 10 km up the valley as evidenced by the relatively high fluxes of F and Mn(total) at location 16 (about 10 and 5 times higher than the intended 'background' levels). The gaseous F and submicron particles are most likely to be deposited by rainout and washout.

The distributions of Al, F, Mn(total) and Fe from the industrial area appear to extend to the other side of the river, as evidenced by the rather high mean deposition rates of these elements at location 13 (about 2 to 5 times higher than the intended 'background' levels). Apart from the influences of the predominant NW and SE winds, which channelled up and down the valley throughout the year, the industrial area is frequently affected by the NE wind flowing from the saddle between Mt. George and the Tippogoree Hills, particularly from late

night to early morning (the frequency of occurrence varying from 26% at 2100 hours to 11% at 0600 hours from December 1982 to November 1983)(2). While this wind could be katabatic, which occurs most frequently in colder months, as characterised by its low speeds (generally <2.0 m/s) and shallow depth (<100 m), it could also be due to the channelling of the lower part of the synoptic winds, notably the easterlies in summer, by the saddle (in this case, the wind speed would be much higher - between 3.4 and 7.9 m/s). The predominance of either wind depends largely on the synoptic conditions of the day. The NE katabatic or channelled winds could transport the air emissions from the industrial area to the Beauty Point and Ilfraville areas where vegetation damage had been first reported in the early 1960s.

Additionally, the industrial area is also influenced by the SW katabatic winds originating from one of the larger side valleys close to Ilfraville frequently cross the river and reach Point Effingham as light SW flows (the frequency of occurrence varying from 15% at mid-night to 11% at 0300 hours in winter 1983)(2). If the main valley is calm, the katabatic winds continue to spread out and reach the industrial area as light westerlies or west-northwesterlies, with a depth of at least about 50 m. Katabatic winds could carry air pollutants in higher concentration, hence more detrimental to the physical and human environment, especially when the winds become moist as they cross over the river during cold, calm and foggy nights or mornings (surface inversions are most likely to develop under these stable conditions). A total of 51 fog days was observed at Bell Bay from September 1982 to August 1983.

The ratio of insoluble to soluble Mn at each sampling location was also determined. Higher ratios (>2.0) were found near to Temco. This implies that the coarser Mn particles which settled near the source were less soluble than those airborne submicron particles, which have longer residence times and could be transported much further away.

The spatial variations of the fluxes of Al, F, Mn(total) and Fe are best illustrated in Figure 2. The contours were drawn by a Zeta 1453 drum plotter using the Surface II graphic system (7). The distribution patterns of Al and F were rather similar, while those for Mn(total) and Fe varied possibly due to the influence of other local sources on the deposition of Fe. In general, the distributions of these elements appear to reflect, to some extent, the major wind flows experienced in the industrial area, especially NW, SE, and NE winds. The different features of the distribution between each element were probably due to the different locality of the emission sources and the different particle size distribution with respect to the meteorological conditions, especially the wind vectors. For example, the SW distribution pattern is more evident for Al and F than Mn(total) and Fe because Comalco is closer to the saddle between Mt. George and the Tippogoree Hills than Temco, hence it is more in the pathway of the NE winds flowing down the saddle.

The Pearson correlation coefficients (r) and the test of significance (p) between the fluxes of any two elements were determined using SPSS (8). Al and F, insoluble Mn and soluble Mn, Fe and Mn (both insoluble) are all significantly correlated, with $p<0.003$. Al is also significantly correlated with insoluble Mn and Fe, with $p<0.001$, indicating that Comalco may not be the only source of Al, or Temco may not be the only source of Mn and Fe. However, unlike Al, F is not significantly correlated with Mn (both soluble and insoluble) and Fe. This indicates

that F is the best tracer for the emissions of the aluminium smelter. Pb, a major emission from motor vehicles, is also included for comparison, and is found only correlated with Fe at $p < 0.001$.

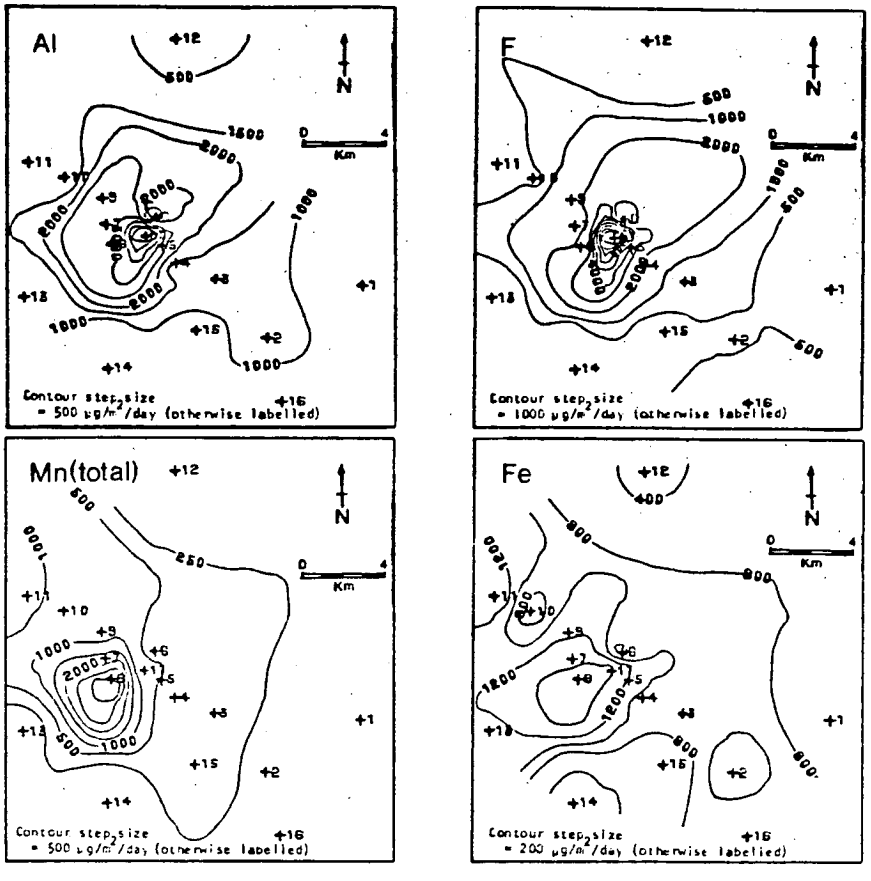

Figure 2. Spatial variations of the deposition of Al, F, Mn, and Fe ($\mu g/m^2/day$) at the 17 sampling locations in the lower Tamar Valley.

Acidity of the Deposition Samples

The pH of the monthly bulk deposition samples (from July 1982 to August 1983) varied from location to location, and ranged from 4.0 to 8.0. For 61 out of 194 samples (or 31.4%) measured there was pH <5.6, a reference most commonly used to define 'acidic' precipitation (9). Of these, 25 samples (or 12.9%) had pH <5.0 (excluding contaminated samples).

It appears that some locations along NW (i.e. 4,6,10) and SE (i.e. 3, 16) of the thermal power station had higher frequency of collecting acidic samples. Of these, location 4, about 1 km NW of the power station and 3 km SE of the industrial area, collected the highest number of acidic samples (10 out of 14). Location 1, about 7 km E of the power station and over the other side of the Tippogoree Hills, had the second highest number (7 out of 13). Air emissions from the 107 m stack of the power station could be transported by the fresh to strong westerly airstreams before being scavenged at the location. Diurnal variations of the westerly winds, as recorded at a location about 3 km NW of the power station, were greatest in summer (frequency of occurrence varying from a minimum of 7% at noon to a maximum of 25% at 2100 hours), and smallest in winter (frequency of occurrence varying from a minimum of 13% at 0600 hours to a maximum of 19% at 1800 hours) (2). All winter months samples in 1983 at location 1 were acidic. Location 14, 5.2 km SW of the power

station, was generally less influenced by the air emissions from Comalco and Temco, as evidenced by the relatively low mean deposition rates of Al, F, Mn and Fe. However, 6 out of 14 samples collected at this location were acidic. Of these, 4 had pH <5.0, including the lowest pH (4.0) measured for the period. It has been observed during the study period that, under stable atmospheric conditions, the plume from the power station failed to penetrate the ground-based inversion of height about 200 m, and bent towards the SW direction possibly due to the influence of the NE katabatic winds originating from the Tippogoree Hills. Indeed, all acidic samples at location 14 were collected in colder months when katabatic winds and surface inversion are most frequent.

Most samples collected near Comalco or Temco (locations 7,8,9 and 17) had higher pH, due presumably to the presence of more alkaline species from the two heavy industries and the concrete mixing plant (e.g. Ca^{2+}, Mg^{2+}). The major acidic species in the lower Tamar Valley are believed to be SO_4^{2-}, NO_3^- and F^-. Possibly some SO_4^{2-} was of marine origin. While both Comalco and Temco are operating 24 hours a day throughout the year, the thermal power station is only operated intermittently. Thus it may be possible to correlate the number of days of the operation of the power station with the number of acidic samples collected. The data collected seem to suggest some such correlation.

Chemical Speciation by FT-IR

FT-IR spectroscopy has been successfully used in air pollution studies in recent years for the identification of chemical components in particulate samples and the trace pollutants in ambient atmosphere (9,10, 11). No analyses of precipitation samples by this technique have been reported in literature, at least in Australia.

The chemical composition of some selected deposition samples, particularly those with low pH, was analysed using a Digilab FTS-20E Fourier transform infrared spectrometer.

One microlitre of distilled water (which was used as a reference) and the filtered sample solution were placed between two AgCl windows 15 mm in diameter (each with a circular depression of 0.025 mm) positioned for 0.025 mm pathlength. The windows were held in a micro mull cell, which was then placed on a rectangular holder. The absorption spectra of the distilled water and the sample solution were obtained with 100 scans at 4 cm^{-1} resolution over the range of 4000-400 cm^{-1} (typically in less than 3 minutes). Figure 3 shows the result of the computer subtraction of the spectrum of the distilled water from that of a sample of pH 4.8 collected in June 1983 at location 4. The resulting spectrum, apart from displaying the absorption bands due to water (1620, 3400, 3688 cm^{-1}), highlights two of the major acid-producing species, namely SO_4^{2-} (670, 940, 1170 cm^{-1}) and NO_3^- (832, 1300, 2460 cm^{-1}). Sulphate has been found to be the only significant form of sulphur in fossil fuel particulate emission samples and is essentially the only anion present in water soluble phase (13). Other chemical species found include NH_4^+ (1400, 1720, 3020, 3280 cm^{-1}), hydrocarbons (2860, 2920, 2970 cm^{-1}), and possibly CN^- (2125 cm^{-1}). Atmospheric CO_2 (2336, 2367 cm^{-1}) was also detected in the spectrum as the gas was not purged before the analysis of the sample. Carbonate (880 cm^{-1}) and the carbonyl group (1,680 cm^{-1}) had also been detected in samples at other locations.

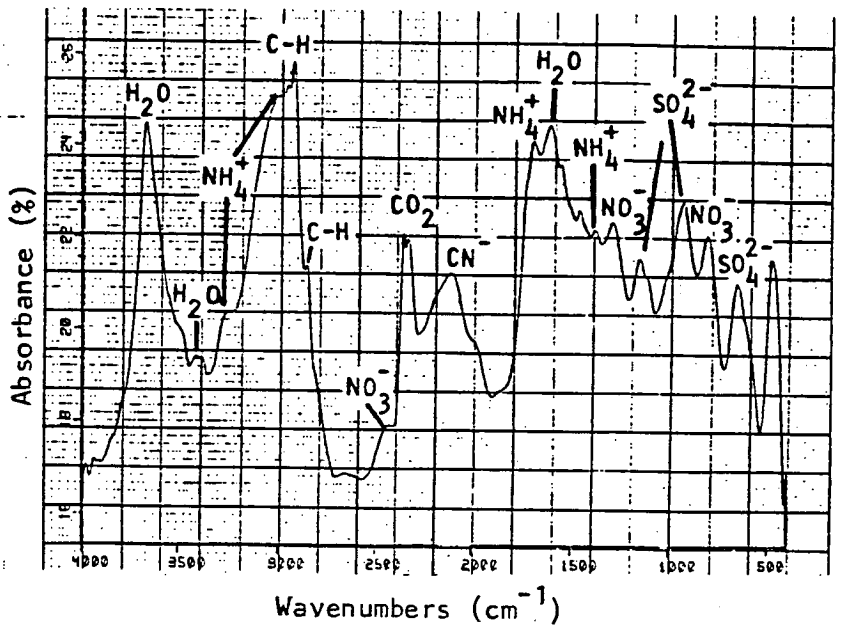

Figure 3. FT-IR absorption spectrum of a precipitation sample (pH 4.8) with background spectrum due to water subtracted.

The identification of the chemical species in the sample was achieved by comparison of the absorption spectrum of the sample with those of standards or literature. It is possible to quantify the concentration of all the chemical species by estimating the infrared band intensities using Beer-Lambert Law.

The application of FT-IR spectroscopy in analysing precipitation samples proved to be a quick and promising technique especially when a good reference library is available for identification of unknown chemical compounds. The technique could be complementary to other elemental analytical techniques such as SEM/EDAX (for solids) and AAS (for solutions).

CONCLUSIONS

The atmospheric deposition samples collected at 17 locations in the lower Tamar Valley from September 1982 to August 1983 were analysed. The mean deposition rates of insoluble dust ranged from 32.4 to 338.3 $mg/m^2/day$. For trace elements Al, F, Mn(total) and Fe, the mean deposition rates ranged from 445 to 5,640, 89 to 12,570, 38 to 3,675, and 392 to 1,535 $\mu g/m^2/day$ respectively. In general, the fluxes of the trace elements were much higher within 3 km of their respective emission sources, but the air emissions from Comalco and Temco could travel at least 10 km up the valley. The spatial variations of the deposition reflect the locality of the emission sources and the particle size distribution of the pollutants with respect to the meteorological conditions, in particular the wind vectors. Statistically, Al and F, as well as Mn and Fe (both insoluble) are found to be significantly correlated.

The pH of the monthly bulk deposition samples (from July 1982 to August 1983) varied from 4.0 to 8.0. The thermal power station appears to be the major source of acid-producing species which could have caused the low pH of some deposition samples. The air emissions from the station could be transported over the Tippogoree Hills by the westerly airstreams. Chemical speciation of precipitation samples by FT-IR was attempted. It seems to be a feasible technique which, with a good

reference library, could be used as a complement of other elemental analytical techniques for the identification of chemical compounds.

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